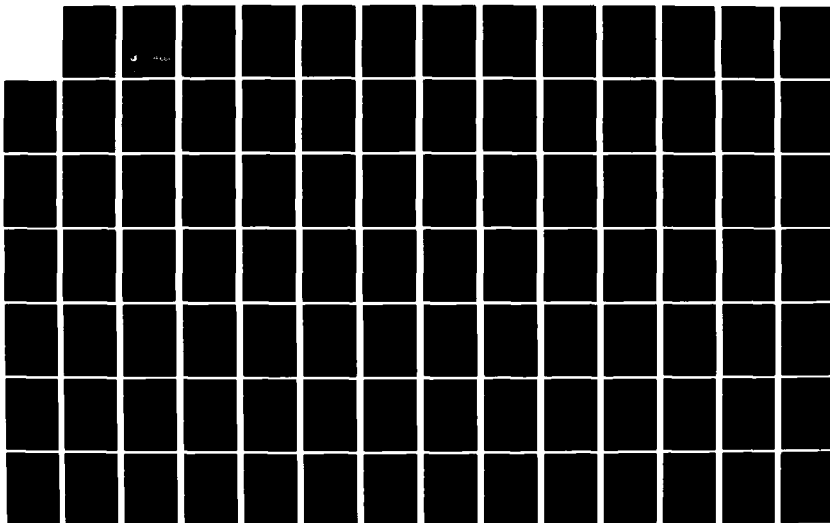


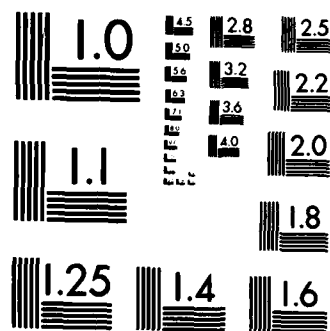
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# THE SECOND CONFERENCE ON THE ENVIRONMENTAL CHEMISTRY OF HYDRAZINE FUELS: 15 FEBRUARY 1979

ENVIRONICS DIVISION  
ENVIRONMENTAL CHEMISTRY BRANCH

APRIL 1982

FINAL REPORT  
15 FEBRUARY 1979

WILLIAM D CHRISTENSEN  
RONALD F HUDSON  
SHERWIN LEWIS, ET AL

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Unsymmetrical Dimethylhydrazine	Environmental Monitoring	Choroinolysis
		Chemiluminescence
20. ABSTRACT (Continue on reverse side if necessary and identify by block number)		
<p>On 15 February 1979, the AF Engineering and Services Laboratory, AFESC, Tyndall AFB, Florida, hosted a conference on the environmental chemistry of the hydrazine fuels. Ten papers were presented on various subtopics, which were:</p> <ul style="list-style-type: none"> <li>A. Environmental Impact and Assissment of Hydrazine Fuel Usage.</li> <li>B. Environmental Toxicology.</li> <li>C. Environmental Monitoring and Disposal of Hydrazines.</li> <li>D. Environmental Modeling and Chemistry of Hydrazine.</li> </ul>		

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1 The subtitles reflect a wide range of subjects. In section A the use of H-70 (70 percent hydrazine) in the emergency power unit of the F-16, hydrazine on the space shuttle, and a fuel transportation risk analysis were discussed. In section B, the toxicity of the hydrazines to selected bacteria and other organisms. This was followed by monitoring of hydrazine fuels vapor by chemiluminescence, and waste disposal by ozonation and chlorinolysis. The conference finished with a presentation on hydrazine spill modeling with estimations of hazard corridors and a summary of environmental physical-chemical properties of the hydrazine fuels.

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## PREFACE

The hydrazine fuels are used in missile guidance systems, as monopropellant fuel on aircraft auxiliary power units, and they will be used by NASA in the space shuttle. Because of the documented toxicity of the hydrazine fuels, it is imperative to have accurate and current information on the potential environmental contamination by these fuels. Data will be required on the environmental chemistry of these compounds in order to develop effective control procedures and make realistic predictions on the environmental impact of accidental fuel releases. With this in mind, the purpose of this meeting was to stimulate discussion and information interchange regarding environmental problems with the use, transport, and handling of the hydrazine fuels.

The second Conference on the Environmental Chemistry of Hydrazine Fuels was sponsored by the Engineering and Services Laboratory (ESL), Environics Division, of the Air Force Engineering and Services Center at Tyndall AFB, Florida, on 15 February 1979. ESL directs both in-house and contracted research efforts under Program Element 62601F on environmental problems concerning the hydrazine fuels and serves as the focal point for related DOD sponsored research.

There were about 60 participants at this conference. There were representatives from the Air Force, Army, NASA, universities, civilian research organizations and chemical manufacturers. Attendees heard formal presentations of the papers compiled in this technical report.

This report has been reviewed by the Public Affairs Office (PA) and is releasable to the National Technical Information Service (NTIS). At NTIS it will be available to the general public, including foreign nations.

This report has been reviewed and is approved for publication.

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Paper No. 1

HYDRAZINE AS A MONOPROPELLANT FOR THE F-16 EMERGENCY POWER UNIT

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USAF Occupational and Environmental Health Laboratory

Brooks Air Force Base, Texas 78235

For some of you attending this conference on the Environmental Chemistry of Hydrazine, this is the first opportunity you've had to meet someone from the Air Force's Occupational and Environmental Health Laboratory. I would briefly like to summarize the mission statement of the laboratory so that you can have an understanding of the role which we play in hydrazine associated issues. As you can see from our mission statement, we operate within the guidelines of Force Program Eight funding. Our primary emphasis is in support to base level organizations in the areas of environmental protection, industrial hygiene and radiological health. During 1978 we had several projects involving support to the F-16 Systems Program Office in preparation for F-16 deployment in January 1979 at Hill AFB. In keeping with the title of this particular session in the conference, Assessment of Hydrazine Fuel Usage, one of my objectives will be to provide you an overview of the F-16's application of hydrazine technology. I will also be presenting a summary of the data which we have collected during maintenance of hydrazine equipment on the F-16 and actions which have been taken to control occupational exposures during those maintenance activities. One of the questions

which is invariably asked by people when they first learn of hydrazine's use on the F-16 is, "Why hydrazine?". In essence that is the question that the Vice Commander of Systems Command asked the Aeronautical Systems Division Commander. In response, a Hydrazine Executive Review Group (HERG) was formed in the middle of 1978 to perform a review of the use of hydrazine, and I'll be discussing and presenting some of the conclusions of that review group. An issue which is going to affect all persons using hydrazine is the Surgeon General's development of an occupational safety and health standard dealing with exposure to hydrazine. I'll be summarizing some of the key issues associated with this document and trying to provide you some insight into its impact on your activities.

The F-16 aircraft is a light weight multirole combat fighter. It relies on continuous electric and hydraulic power to maintain flight stability. This technology is referred to as "fly by wire." The significance of this concept to the F-16 lies in the fact that the aircraft has a single engine. Any interruption in either electric or hydraulic power can rapidly induce loss of flight control. For this reason, the aircraft is equipped with an emergency power unit (EPU) which senses any interruption in either electric or hydraulic power and initiates backup power via a turbine and gearbox assembly.

The major components of the emergency power system are shown in this schematic diagram (Figure 1). A cylinder of nitrogen is used

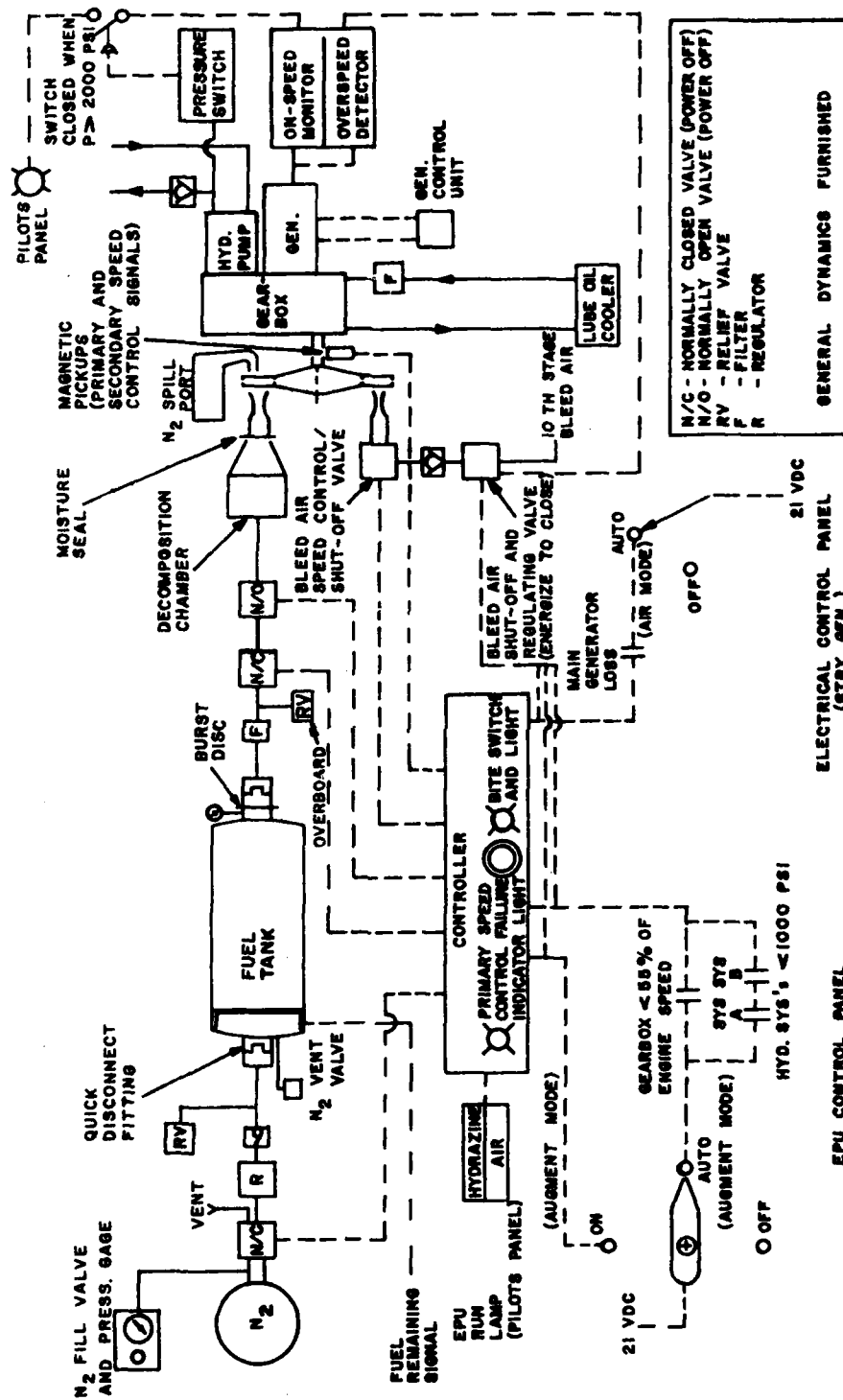


Figure 1. F-16 EPU Schematic Diagram

to pressurize a hydrazine fuel tank. The fuel used on the F-16 is a mixture of 70 percent propellant grade hydrazine and 30 percent water. When the system is pressurized, a burst disk on the hydrazine end of the cylinder ruptures and hydrazine is forced from the EPU tank by a moving piston in the tank. The hydrazine travels to a gas generator where it decomposes on an iridium/alumina catalyst. The gas is used to power up a turbine which is connected to a gearbox. The gearbox drives a hydraulic pump and an electric generator, thus ensuring continuous electric and hydraulic power. In operation, the turbine speeds up to 70,000 rpm in less than three seconds. Later in my briefing I will be discussing some of the maintenance aspects of servicing a fired EPU system, but for a moment let me discuss the Hydrazine Executive Review Group that was formed at the request of the Vice Commander of Systems Command to evaluate the introduction of hydrazine to the flight line environment.

In the spring of 1978, the Vice Commander of Systems Command directed the Aeronautical Systems Division to accomplish a multidisciplinary review of hydrazine related issues. There are many factors which I'm sure contributed to this decision, not the least of which was the publication of the NIOSH criteria document on hydrazines and the proposal by OSHA for a generic cancer policy. To be specific, the Hydrazine Executive Review Group (HERG) was co-chaired by representatives from Aeronautical Systems Division and the Acquisition Logistics Directorate. The task of the HERG was to develop a perspective on the need for hydrazine on Air

Force aircraft, develop a technical assessment of the F-16 hydrazine powered EPU and identify all alternatives to the hydrazine powered EPU if usage was denied in the future. To perform this task, members from several laboratories and operational organizations within the Air Force were called upon to provide their expertise and advice on these issues. A number of sub-groups were formed within the HERG to address each of the issues. These were discussed at length over a period of four months after which the HERG released its conclusions. As far as hydrazine is concerned, it was the HERG's opinion that less toxic substances should be utilized when feasible. However, toxic or hazardous chemicals can be utilized on the flight line when we employ work procedures compatible with occupational health standards. In addressing the F-16 EPU issue, the HERG traced the logic used in the selection of the hydrazine powered unit and examined alternatives to hydrazine technology. The alternatives evaluated included a JP-4/LOX system, an augmented ram air turbine system and a peroxide system. The HERG concluded that hydrazine should not be replaced on the F-16 aircraft but alternative technologies should be pursued in the event such replacement would be required.

1978 turned out to be a very active year for our laboratory in areas associated with hydrazine. In addition to the HERG, Table 1 lists the other projects involving our support which I'll briefly discuss today. We've also been actively involved in the deliberations of the SAMSO propellant working group and the JANNAF. In November of 1977, the F-16 SPO requested our assistance in the

evaluation of potential occupational exposures associated with handling of hydrazine during routine maintenance tasks on the F-16 aircraft. Our first problem was one with which you are all familiar. Given the current stringent criteria associated with occupational exposures to hydrazine, there is no instrumentation which can provide reliable real time concentrations. As a result we reviewed alternative technology for indirect measurements. Our first effort involved the Wood Anderson technique which employs acid impregnated silica gel as a solid sorbent. In preparation for our survey, we tested our technique in San Antonio and to our disappointment, discovered that these tubes were very sensitive to humidity. During the first 10 to 15 minutes after installation, after per minute, the pressure drop increased dramatically resulting in changes to the air flow rate. In addition to the increase in pressure drop, there was a visible change to the character of the sorbent media, which led us to suspect that channeling could be occurring. In discussing these problems with personnel in the School of Aerospace Medicine, we learned that they had been testing fire brick as an alternative substrate for the acid. The fire brick technique was found to overcome some of the limitations of the Wood Anderson substrate and yet provide equal sensitivity and sorbent/desorbent characteristics. Samples collected on the acid impregnated fire brick tubes were analyzed using the para-dimethylaminobenzaldehyde (PDAB) method. This technique is sensitive at the microgram level and proved very satisfactory for our purposes of occupational evaluations. The second problem we

were faced with was a review of the procedures to be used on the F-16 and identification of those tasks during which exposure to hydrazine could occur. The maintenance tasks in Table 2 are the ones which we eventually identified as being the ones which presented the highest probability for exposure. They are tank depressurization, catalyst purge, and poppet valve replacement. All these tasks take place on the aircraft. The tank which contains the hydrazine is removed from the aircraft for servicing in a specialized facility, and so an additional area of investigation was the EPU tank servicing area.

TABLE 1. USAF OEHL SUPPORT TO THE F-16 PROGRAM (1978)

HYDRAZINE EXECUTIVE REVIEW GROUP (HERG)  
F-16 MAINTENANCE TASK EXPOSURE EVALUATION  
F-16 REFILLING STAND EXPOSURE EVALUATION  
AFOSH STANDARD ON HYDRAZINE

TABLE 2. USAF OEHL TASK EVALUATION

- A. USAFSAM FIREBRICK TECHNIQUE WITH PDAB ANALYSIS
- B. ON-AIRCRAFT MAINTENANCE TANK DEPRESSURIZATION  
CATALYST PURGE POPPET VALVE REPLACEMENT
- C. EPU TANK SERVICING

In January 1978 a survey involving both aircraft and tank servicing tasks were performed. Based on the results of our tank servicing study in January, we accomplished a resurvey in October 1978 after modifications had been accomplished to the servicing equipment. In general, you can see that the results of the expo-

sures are well below permissible exposure limits (Table 3). These exposure concentrations are presented in terms of the period required to perform the task and not on an 8-hour TWA basis. On that basis, obviously we would have much lower concentrations. With regards to tank servicing, you'll see from the footnote that we did identify areas in which peak exposures from 5 to 8 part per million could occur during short periods of time. As a result of that, modifications were made to the device used to service these tanks. The follow-up survey conducted in October 1978 did not identify these peak excursions.

TABLE 3. SURVEY DATA

	<u>JANUARY 1978</u>	<u>OCTOBER 1978</u>
	MEAN CONCEN. (PPM)	MEAN CONCEN. (PPM)
ON AIRCRAFT	0.03	
TANK SERVICING	0.04 to 0.16*	0.004 to 0.012

\*POTENTIAL PEAK EXPOSURE AT 5 AND 8 PPM

NOTE: THE TWA FOR HYDRAZINE IS 0.1 PPM WITH EXCLUSIONS NOT TO EXCEED 0.3 PPM IN ANY 15 MINUTES.

On the basis of the survey results, we have been able to identify task-specific protective equipment for use by maintenance technicians during the individual tasks for which they may have potential exposure to hydrazine. In general, this equipment is designed to prevent both skin absorption and inhalation of hydrazine. I am pleased to say that the engineering modifications recommended in our technical reports have been implemented by the F-16 program office (Table 4). The first modification you see

deals with the on aircraft servicing called depressurization. Since the EPU tank utilizes a wetted wall piston, it is possible for some hydrazine vapors to be on the nitrogen side of the tank, and so when the tank is depressurized, it is essential to remove hydrazine vapors from the nitrogen. As a result of the January study which identified this as potential problem area, General Dynamics designed a scrubber system for use during nitrogen depressurization. The efficiency of this scrubbing device has been certified by the Civil and Environmental Engineering Development Office (CEEDO). The second engineering modification deals with the changes made on the stand used for refilling of the EPU tanks. The most significant modification made to that equipment again dealt with a scrubber system installed to remove hydrazine from the vent gases during refilling operations. The final recommendation outlines a total occupational medicine program oriented towards exposures to hydrazine. This recommendation tied in very closely with the project which the Surgeon General's office initiated, referred to as an Air Force Occupational Safety and Health standard on hydrazine.

TABLE 4. RECOMMENDED ACTIONS

- A. TASK-SPECIFIC PROTECTIVE EQUIPMENT
- B. ENGINEERING MODIFICATIONS AIRCRAFT SCRUBBER  
ASSEMBLY REFILLING STAND MODIFICATIONS
- C. OCCUPATIONAL MEDICINE PROGRAM

Because of the heightened concern for the toxicology of hydrazine and the fact that we are moving from a relatively controlled popu-

lation of occupational exposed individuals to a more diverse population, the Surgeon General's office identified the need for uniform guidance to all medical personnel confronted with the evaluation of persons exposed to hydrazine (Table 5). This standard will specify a permissible exposure limit and outline the requirements of an occupational medicine and industrial hygiene surveillance programs to be employed at all bases where hydrazine is used. A few qualifying comments are required at this point. To begin with, the standard has not been implemented at this time. It has been provided as interim guidance to those major commands using hydrazine, and will be reviewed March 1979 to determine their experience with this proposed standard and incorporate their comments on the standard before it is finally published. One of the unique characteristics dealing with this AFOSH standard will be the fact that it will contain supplementary information for various weapons systems. The proposed standard contains a supplement of the F-16 program. It outlines some of the unique characteristics of the aircraft and provides specific information for medical personnel who are confronted with F-16 issues. In addition to the F-16 supplement, HQ SAC is preparing a Titan supplement which will be incorporated in the standard. HQ MAC has also been tasked to prepare a supplement dealing specifically with the transportation of hydrazine materials. These are areas which I'm sure many of the people in our audience will be coming very much involved in over the next few months.

TABLE 5. AIR FORCE OCCUPATIONAL SAFETY AND HEALTH STANDARD FOR  
HYDRAZINE

- A. USAF/SG POLICY ON CONTROL OF HYDRAZINE EXPOSURE
- B. PERMISSIBLE EXPOSURE LIMIT
- C. UNIFORM OCCUPATIONAL MEDICINE AND INDUSTRIAL HYGIENE  
SURVEILLANCE PROGRAMS
- D. F-16 SUPPLEMENT

Finally, I'd like to identify from our perspective those issues which remain unresolved as they relate to hydrazine and the F-16 program (Table 6). I think you'll realize that many of the issues which we are concerned about are issues which we all share in common. In general we are concerned with the lack of toxicology information on the oncogenicity of hydrazine and the potential of skin absorption of the vapor. It is obvious that we would all desire to have detection and monitoring equipment which could be real time and provide a personal dose exposure for each individual. While the F-16 program is using relatively small amounts of hydrazine in comparison to other programs, such as the Titan, control of hydrazine during transportation and disposal of spilled hydrazine present significant problems. This becomes particularly true when one considers the problem of decontamination of an aircraft in which hydrazine has been spilled.

TABLE 6. UNRESOLVED ISSUES IMPACTING F-16 PROGRAM

- A. TOXICOLOGY  
ONCOGENECITY OF HYDRAZINE  
SKIN ABSORPTION OF VAPOR
- B. DETECTION AND MONITORING  
PERSONAL DOSIMETER  
REAL-TIME AREA MONITORING
- C. CONTROL AND DISPOSAL  
TRANSPORTATION  
NEUTRALIZATION

My purpose in being here today is to provide you insight into the progress which has been made in controlling exposures to hydrazine on the F-16 program. I've been discussing some of the issues which have come up over 1978 which have implications for all hydrazine users. It is my belief that the liaison which our laboratory has had with the F-16 program has been highly productive. Many of the issues which we have addressed and resolved over this past year are ones which traditionally would not be uncovered until the deployment of the aircraft system. At this point I'd like to yield any time I have remaining for questions you may have on areas which I have been discussing.

PAPER NO. 2

ENVIRONMENTAL IMPACT PROCESS AND HYDRAZINE FUELS FOR  
AIR FORCE SPACE SHUTTLE PROGRAM

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ABSTRACT

An overview of the Environmental Impact Statement process and time frames for Space Transportation System (STS) construction and launch activities at Vandenberg AFB are presented. Hydrazine and monomethylhydrazine (MMH) are used as hypergolic fuels in the Space Shuttle Orbiter and its solid rocket boosters. Between 13,000 and 27,000 pounds of the fuel are used for each launch. Characterization of hydrazine disposal effluent is necessary in order to satisfy state and local air pollution, water pollution, and solid waste regulations governing Vandenberg AFB. Possible spills and long-term storage requirements are areas of concern requiring additional environmental impact analysis.

SAMSO ENVIRONMENTAL PLANNING

The organization of our environmental group with SAMSO is shown in Figure 1. Under the Commander, Vice Commander, and Chief of Staff

are the major parts of SAMSO; deputies (i.e., Deputy for Reentry Systems), units (i.e., Space and Missile Test Center, SAMTEC, at Vandenberg AFB), and staff officers (i.e., Directorate of Civil Engineering, DE). DE includes engineers, construction project managers, support personnel, and the environmental planning division (DEV). This division (DEV) has six staff members and a supervisory engineer, who is also the environmental coordinator (EC) and chairman of the SAMSO Environmental Protection Committee (EPC). The EPC is the working group and has authority for (through the chairman) environmental matters. As a minimum the committee is composed of representatives from the following staff functions: Weather (WE), Safety (SE), Information (OI), Legal (JA) and DEV. Technical advisors and other staff offices are also represented on the committee as appropriate for a particular project. Being a large organization SAMTEC has its own EPC, and SAMTEC representatives do attend SAMSO EPC meetings (and vice versa) as appropriate. AF Systems Command also has an environmental protection committee, and major SAMSO environmental documents, including formal environmental assessments/statements must have both SAMSO EPC and AFSC EPC approval.

#### SPACE SHUTTLE ACTIVITY

Our office, DEV, is the designated authority for all Air Force Space shuttle environmental matters. The environmental studies and statements in support of Vandenberg and Port Hueneme Space Shuttle activity are contracted and managed through our office.

The location of the Vandenberg Space Shuttle facilities is shown in Figure 2. Ground breaking for first construction was accomplished early in 1979. Approximately 300 million dollars worth of construction is programmed before the first launch in 1983. The facilities to be built at VAFB include runway extension, orbiter servicing and processing facilities, launch pad modifications, road widening and new road for tow route, and a harbor landing facility. Fuels, especially hydrazine, are handled and stored at a number of these facilities (described later). The construction involves considerable land impacts, air and water emissions, and a large workforce with resultant socioeconomic impacts. Operations produce emissions, noise, and other impacts. Thus the effort required for environmental considerations and resultant mitigations is considerable. This environmental program is outlined in Table 1.

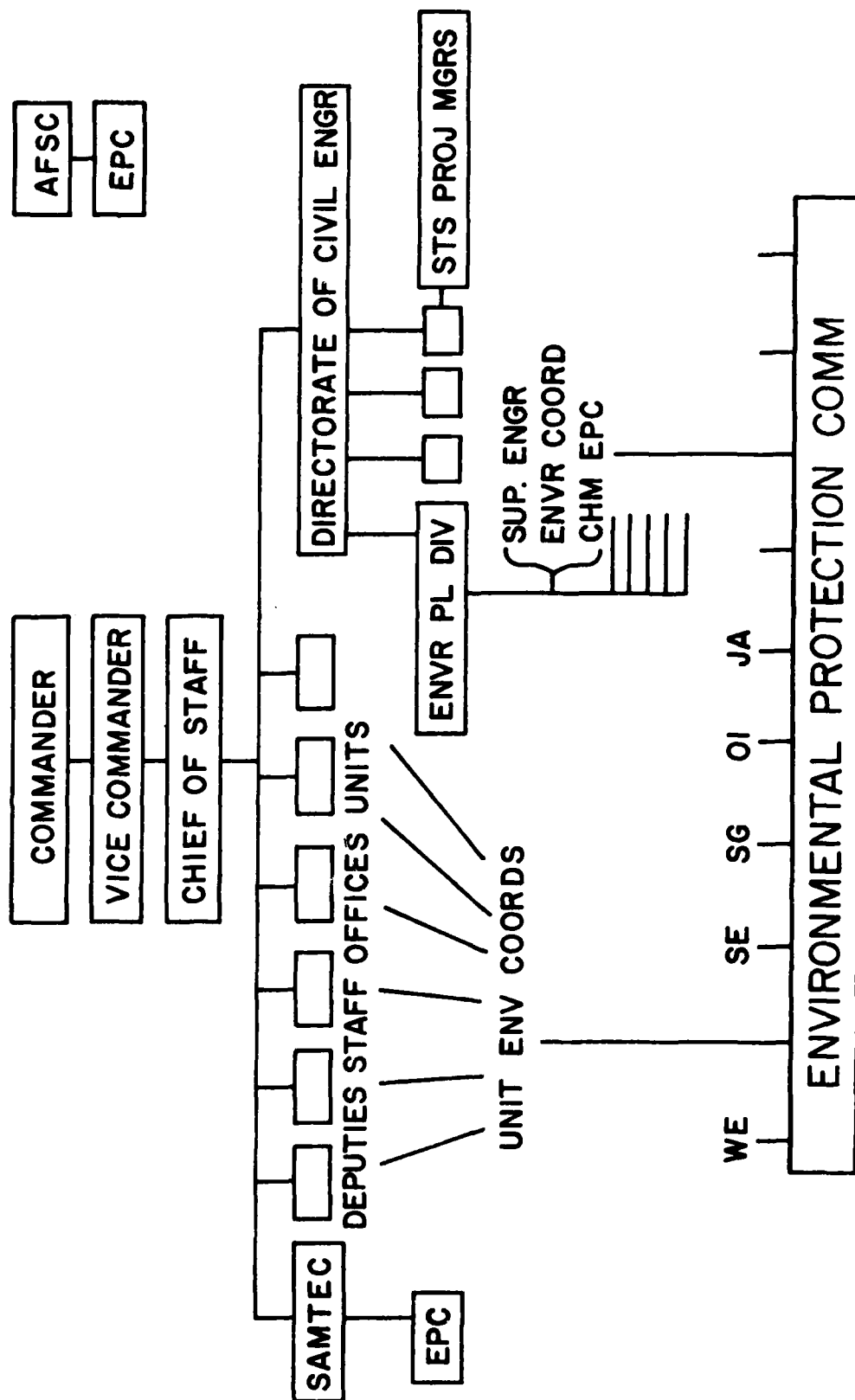


Figure 1. SANSO Environmental Structure

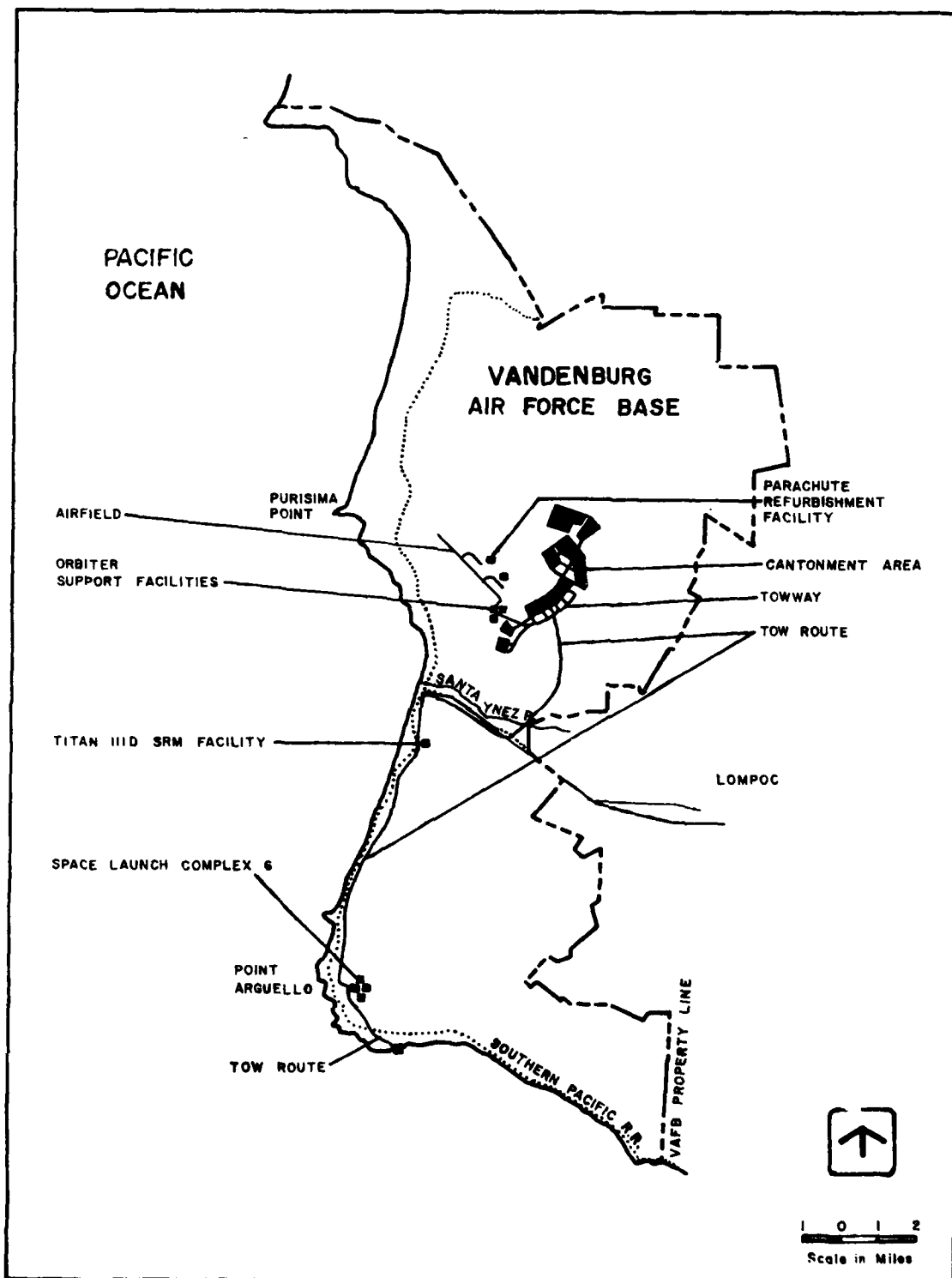


Figure 2. Location of proposed Space Shuttle Facilities at Vandenberg Air Force Base.



determine statement requirements and tasking for the process. It was decided that a full statement would be required, and SAMSO/DEV was tasked with the job. This EIS (reference 1) covered all ground activities associated with STS at VAFB and Port Hueneme including construction and operation, to within a few minutes after takeoff. Upper atmosphere effects and U.S. overall effects (such as development of the orbiter) are covered in the NASA Space Shuttle EIS (reference 2).

Next, baseline studies were conducted in order to provide data for the EIS and to provide input for siting and other decisions. Separate studies were accomplished by various contractors for the following areas of impact: biology (an inventory of the entire base was accomplished, reference 3); endangered species (plants were surveyed at construction sites, reference 4); archaeology (over 400 sites exist on VAFB, reference 5); marine biology and oceanography (for an external tank landing facility, reference 6, and 7); and socioeconomics (reference 8).

A Draft Environmental Impact Statement (DEIS) was then prepared. Information was utilized from the baseline studies, facility design proposals, field trips, engineering data and many other sources. Coordination was accomplished with state and local government agencies both before and after publishing of the DEIS. For example, floor tiles from the La Pruisima Mission in Lompoc were tested to alleviate concern that they may be subject to breakage from the descent sonic booms.

Preparation of the DEIS required many months of contractor and DEV effort. Command and Headquarters comment with a number of subsequent changes was necessary before approval and the DEIS was released to the public in August 1977. A notice of its release was published in the Federal Register, and over two hundred copies were sent to public agencies, private individuals, and libraries. A 45 day review period to provide opportunity to comment was established.

A public hearing date was set and on 28 September 1977 the hearing was held in Lompoc, CA (next to VAFB). All those who wished to were given the opportunity to express any concerns or comments. Their questions were answered at the hearing or by letter afterwards and the entire hearing transcript then was printed as an appendix of the FEIS.

Public and agency comments were then collected and responses prepared. Changes in plans for a number of the facilities had been made, material was added, and changes were made to the FEIS to satisfy the comments. The FEIS, now over 600 pages long, was released to the public in February 1978.

The FEIS certainly was not the culmination of the STS EIAP. Some issues came to light during public comment period but could not be treated thoroughly in time for the FEIS. These matters required considerable additional study and their results will appear in an EIS supplement, planned for approximately February 1980. Studies which were not completed for the FEIS or commenced afterward are:

marine biology (a thorough study of the boathouse area), archaeology (additional surveys and results of excavations), sonic boom (effect on Santa Barbara Channel Islands), monitoring plan, updated socioeconomic study, and air pollution emissions inventory. The last item is to be used to assist in the determination of any air quality assessment of permits necessary.

The EIS supplement will cover facilities updates, the results of the aforementioned air pollution work, and the results of other studies completed post-FEIS.

The next phase of the EIAP is the Environmental Protection Plan (EPP) for each STS facility. These plans were developed as part of the ground and support services integration (GSSI) work done under contract to SAMSO. Primary purpose of the EPP is to provide environmental protection information to criteria and specification preparation engineers. The EPP contains information necessary to the architect-engineer in order to plan facilities and equipment in a manner consistent with program environmental goals both during construction and during operation. Secondary goals of the EPP are to ensure environmental awareness, assure compliance with environmental standards, and assist in EIAP considerations throughout the life cycle of the program.

The EPP follows this general outline:

- a. Station set description
- b. Significant environmental features (such as endangered species nearby)

- c. Environmental regulations and importance matrix
- d. Environmental effects
- e. Mitigation measures, causative action, effect
- f. Indirect effects and mitigation measures
- g. Unresolved issues
- h. Coordination and consultation referrals
- i. Data references

A set of 105 general mitigation measures have been worked out for STS construction and operation. The proper measures that are applicable to a particular station set are then referenced in the EPP. An example is mitigation measure number G3:

Surface runoff water or other water containing biologically harmful substances from construction sites shall be treated to meet applicable standards.

The next step for the incorporation of environmental concerns is in the design specifications. The project manager interfaces with DEV and GSSI environmental contractor as necessary during the development of the specifications. After award of the design contract to an architectural-engineering firm (A-E), the 30 percent, 60 percent and 90 percent design submittals are reviewed by DEV and discrepancies worked out with the design agent (usually the Corps of Engineers), project manager, contractor and DE. A

contractural requirement is that the design specification incorporate mitigation measures from the EPP. To assure this, an environmental implementation plan is included as part of the design document. The A-E firms competing for the construction contract will then take into account the environmental measures in their project bid. During construction, monitors from the A-E, Corps of Engineers, GSSI contractor, base, or DEV as specified are available to manage environmental concerns or unexpected problems (such as uncovering an archaeological value, i.e., Native American artifact).

During operations environmental monitoring is planned (such as biological monitoring for possible launch exhaust cloud effects). Of course, this phase is years away as the first launch is planned for late 1983.

#### HYDRAZINE AND THE SPACE SHUTTLE

Monomethylhydrazine ( $\text{CH}_3\text{NHNH}_2$ , MMH) oxidized by nitrogen tetroxide ( $\text{N}_2\text{O}_4$ ) provides thrust to the orbiter vehicle after its main thrust fuels are expended. This occurs a few minutes after launch. The main thrust is provided by liquid hydrogen and liquid oxygen fed to the orbiter main engine from a large external tank (ET) which is jettisoned into the South Pacific and from two solid rocket boosters (SRB's) which are recovered for re-use 150 miles down range. Hydrazine monopropellant ( $\text{N}_2\text{H}_4$ ) is also used in auxiliary power units in the orbiter and SRB's.

MMH and  $N_2O_4$  are hypergolic bipropellants; that is they ignite spontaneously when put into contact with one another. Anhydrous hydrazine (AH), a monopropellant, ignites spontaneously when it contacts a catalytic bed.

The MMH/ $N_2O_4$  is the only source of thrust when the shuttle vehicle is in orbit. Small rocket engines enable fine adjustments in positions; larger ones enable extensive maneuvering and kicking out of the orbit. The orbiter payload may contain hydrazine for any required orbital changes or for boost into higher orbit (payload bay kits).

Quantities of hydrazines carried by the orbiter for the different systems appear in Table 2. Between 13,000 and 27,000 pounds of the two hydrazines are used in each launch.

TABLE 2. SPACE SHUTTLE PROPELLANTS

A. LAUNCH PROPELLANTS

1.  $\text{LO}_2/\text{LH}_2$  EXTERNAL TANK - ORBITER MAIN ENGINES
2.  $\text{Al}/\text{NH}_4\text{ClO}_4$  SOLID ROCKET BOOSTERS (2)

B. ORBIT PROPELLANTS -  $\text{MMH}/\text{N}_2\text{O}_4$  - THRUSTERS

1. FORWARD REACTION CONTROL SYSTEM	FRCS	2,841 lb
2. AFT REACTION CONTROL SYSTEM (L&R)	ARCS	
3. ORBITAL MANEUVERING SYSTEM (L&R)	OMS	9,517 lb
4. PAYLOAD BAY KITS	PB	<u>14,160 lb</u>
		26,518 lb max

C. AUXILIARY POWER UNITS -  $\text{N}_2\text{H}_4$

1. ORBITER
2. SRB f 1,000 lb

In addition to the orbiter and launch pad where it is fueled, ground facilities that service the orbiter vehicle and its components have hydrazine processing areas. The individual facilities include fixed storage tanks, parked tank trailers, portable service units, piping and vent lines, vent gas scrubbers, waste tank trailers, contaminated fuel tanks, spill trenches and ponds.

TABLE 3. HYDRAZINE GROUND FACILITIES

- A. LAUNCH PAD
- B. SAFING AND DESERVICING FACILITY
- C. ORBITER MAINTENANCE AND CHECKOUT FACILITY
- D. HYPERGOLIC SERVICE FACILITY (A&B)
- E. SRB DIASSEMBLY - PORT HUENEME
- F. SRB REFURBISHMENT

Problems facing the Space Shuttle related to hydrazine are representative of problems faced by manufacturers and users of other toxic substances today. Increased numbers of government health agencies and public concern about toxic substances and hazardous wastes are the results of pollution disasters such as with kepone, PBB's in Michigan cattle, PCB's in the Hudson River, and the Love Canal in New York. Too often in the past generators have evaded responsibility for toxic and hazardous substances yet government agencies and the public have paid dearly because of their effects. The result has been a dramatic increase of restrictive regulations governing these and other pollutants.

ENVIRONMENTAL LAWS AFFECTING HYDRAZINE USAGE

The Toxic Substances Control Act (TSCA) places an increased burden on manufacturers of harmful substances. For instance strict records and inventories are now required and new hazardous waste and carcinogen regulations have been proposed; the new regulations will undoubtedly affect hydrazine use. A significant potential problem is the demonstrated carcinogenicity of hydrazines in

laboratory animals. If the hydrazines are classified as carcinogens, the new regulation could require extensive protection for workers. The resultant protective measures would add considerable cost to the STS program. Such measures which may be required for hydrazine handlers are constant detection and monitoring, special protective clothing, showers, medical surveillance and examinations, keeping of records for 30 years, signs and alarms.

Presently detection and monitoring equipment is being tested for STS use. Indications now are that an adequate, reliable and reproducible system is apt to be very costly. The requirements for control of hydrazine vapors are established by OSHA (Occupational Safety and Health Administration), NIOSH (National Institute of Occupational Safety and Health), and resultant Air Force Occupational and Health (AFOSH) standards. Workplace concentrations are set forth in these standards. Current Air Force standards of 0.1 ppm for hydrazine and 0.2 ppm for MMH are under review and may go lower in the future. The hydrazines also appear on the "extremely hazardous waste" list in the California Health and Safety code (Title 22, division 4, section 60283). Permits and record keeping procedures are required for disposal of such waste. Waivers may be granted provided the operator proves the processed waste is rendered harmless.

Santa Barbara County regulations require that a permit be applied for the construction and operation of any device that emits air contaminants. Thus hydrazine would be included.

Liquid wastes, emanating from a hydrazine scrubber, are regulated by water pollution laws. It is unlikely that any land discharge of such waste would be allowable.

AFR 19-1 specifies that as a matter of Air Force policy environmental pollution is to be minimized. Impact on the environment must be analyzed by writing an environmental assessment of EIS as per AFR 19-2.

Recent solid waste, water pollution and air pollution legislation specified compliance by Federal agencies in those areas of state and local standards. This change (Federal agencies were previously exempt from applying for permits) was reiterated and expanded by Executive Order 12088 mandating compliance with all applicable Federal, state and local environmental pollution laws; the same as any non-government entity. In other words, the Air Force is not exempted in the name of national defense (except by special Presidential exemption). All these regulatory concerns are outlined in Table 4.

TABLE 4. REGULATIONS

- A. AFR 19-1, 19-2, OTHERS
- B. OSHA, AFOSH           .2 PPM MMH (NO EXCEEDANCE)  
                          .1 PPM N<sub>2</sub>H<sub>4</sub>
- C. WATER POLLUTION
- D. SANTA BARBARA COUNTY
- E. STATE OF CALIFORNIA
- F. TSCA
- G. CAAA 1977 AND E.O. 12088
- H. PROPOSED CARCINOGEN REGULATIONS
  - 1. MONITOR
  - 2. ALARMS
  - 3. CLOTHING
  - 4. SHOWERS
  - 5. SIGNS
  - 6. MEDICAL SURVEILLANCE
- I. PROPOSED HAZARDOUS WASTE REGS

As a summary space transportation system hydrazine concerns are presented in Table 5. Resolution of these concerns may be effected by proper coordination of Air Force organization and public agencies, accompanied by manpower and funds appropriations.

TABLE 5. STS HYDRAZINE ENVIRONMENTAL CONCERNS

- A. WORKER EXPOSURE
- B. PUBLIC EXPOSURE
- C. AIR POLLUTION PERMITS
- D. COST TO SHUTTLE PROGRAM
- E. DISPOSAL OF WASTES
- F. BURNER/SCRUBBER DECISIONS
- G. CLOTHING - SCAPE SUITS
- H. SPILLS
- I. TRANSPORTATION CONTINGENCIES
- J. DETECTION AND MONITORING
- K. STORAGE PLAN/MANUFACTURING
- L. FUTURE REQUIREMENTS
- M. DUTY TO PROTECT PEOPLE AND ENVIRONMENT

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PAPER NO. 3

## STORABLE ROCKET FUEL TRANSPORTATION RISK ANALYSIS

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### Hydrazine Propellants:

The Air Force hydrazine fuels, anhydrous hydrazine, monomethylhydrazine, and unsymmetrical dimethylhydrazine are transported between Lake Charles, LA; Denver, Colorado; Cape Canaveral, Florida; and Vandenberg Air Force Base, California as well as SAC sites throughout the country. Historically the Air Force has annually shipped an average of 5.2 million pounds of amine fuels over 150,000 miles of rail and highway. Although to date there has been no major mishap during transportation, there is a finite probability that a 68,000 pound rail car or a 40,000 pound truck trailer could be involved in an accident in which the hydrazine fuel, a suspect carcinogen, is released into the environment. The purpose of this study was to quantify the probability of such an accident in the next ten years.

In the period of 1971 through 1977, there have been a total of eight Hazardous Materials Incident Reports made to the Department of Transportation involving the three hydrazine fuels and  $N_2O_4$  oxidizer. Six of the reports involved leaky 55 gallon drum containers, one report involved a pinhole leak in a rupture disc on a  $N_2O_4$  tank truck, and one involved an empty  $N_2O_4$  tank truck

trailer that was overturned on a slippery highway in Abilene, Texas in September 1973.

With such sparse accident data it was decided to utilize all available truck and train accident data to establish a theoretical model. Much of the data used was derived from sources recommended by William A. Probst, Chief, Transportation Branch U.S. Atomic Energy Commission, Washington, D.C. Total train accidents tabulated by the Department of Transportation from 1969 through 1976 are listed in Table 1. The monetary reporting threshold was changed in 1975 from \$750 to \$1,750. The total number of accidents reported, averaged from the low 7,000s to the mid 10,000s during the reporting period. Data compiled for the same period by the Interstate Commerce Commission Bureau of Economics indicated that the total freight car miles averaged from 30.4 billion freight car miles to a low of 27.6 billion freight car miles. Assuming that the average accident involves ten rail cars we derive an accident rate in cars per million car miles that stayed relatively constant between 1969 and 1972 at about 2.7 and appears to be rising to the 3.7 rate in 1976. The Department of Transportation data indicates that about 70 percent of the train accidents were derailments and 21 percent were collisions.

TABLE 1. SUMMARY OF FREIGHT CAR ACCIDENTS

	Total Train <u>Accidents</u>	Freight Car <u>Miles<sup>(5)</sup> x 10<sup>-9</sup></u>	Accident Rate <sup>(6)</sup> Cars <u>Per Million Car Miles</u>
1969	8,543 (3)	30.4	2.8
1970	8,095 (1)	29.9	2.7
1971	7,304 (1)	29.2	2.7
1972	7,532 (2)	30.3	2.5
1973	9,698 (2)	31.2	3.1
1974	10,694 (2)	30.7	3.5
1975 (4)	8,041 (2)	27.6	2.9
1976	10,450 (3)	28.5	3.7

1. Department of Transportation 6th Annual Report, Page 198
2. National Transportation Statistics, DOT-TSC-OST-77-68, Page 88
3. Congressional Subcommittee Hearings on DOT, Page 813
4. Monetary reporting threshold was changed in 1975 from \$750 to \$1750
5. Transport Economics ICC Bol. D, No. 2 1978, Page 19
6. Assumes an average of ten cars involved in any accident.

Truck accident data are not totally documented as are train accidents. However, in any given year approximately 20 percent of the total number of carriers authorized by the Interstate Commerce Commission are part of a reporting system that account for 95 percent of the total mileage of authorized carriers. Authorized carriers account for more than 75 percent of the reported interstate accidents of which about 55 percent of these accidents

are collisions. From 1966 through 1972 the accident rate per million vehicle miles remained relatively constant (Table 2). However, considering the inflationary effect on the cost of truck parts, the safety record was probably improving. This was confirmed by the 1973 data. When the reporting minimum was increased to \$2,000 the accident rate dropped dramatically. A 1973 \$2,000 minimum accident is probably more representative of one in which a propellant spill is more likely to result.

Although the data were no longer available after 1973 for trucks and 1976 for trains, the final results were probably not affected significantly. The fact that rail is trending up while truck is trending down tends to compensate the results. On best available data then we can forecast a rate of .95 million vehicle miles.

TABLE 2. SUMMARY OF "FOR-HIRE" TRUCK ACCIDENTS (1)

	<u>Carriers Reporting</u>	<u>Total Truck Accidents</u>	<u>Total Vehicle Miles x 10<sup>-9</sup></u>	<u>Accident Rate Per Million Vehicle Miles</u>
1966	2,975	26,606	11.0	2.42
1967	2,811	25,981	10.7	2.43
1968	2,734	29,209	11.7	2.50
1969	2,753	30,672	12.5	2.46
1970	2,975	33,203	12.4	2.68
1971	2,928	30,581	14.0	2.19
1972	3,050	36,682	15.9	2.31
1973	3,179	20,560 <sup>(2)</sup>	21.6	0.95

1. All data from Accident of Motor Carriers of Property DOT Bureau of Motor Carrier Safety
2. Monetary reporting threshold was changed in 1973 from \$250 to \$2,000

With a reduction and elimination of Titan engine acceptance firings and development firings the past average movement of 5.2 million pounds of hydrazine fuels will drop considerably. The Titan booster, which is the primary user of Aerozine-50 is scheduled to be phased out in favor of the Space Shuttle. Space Shuttle uses cryogenic main propellants, but does use the hydrazine fuel MMH for auxiliary propulsion. Table 3 is a ten year forecast of the total Launch Vehicle requirement for hydrazine, UDMH, Aerozine-50, and monomethylhydrazine. All other requirements are insignificant by comparison. It is predicted that by 1986 only MMH for the Shuttle vehicle and some small amounts of hydrazine for shuttle and satellite vehicles will be required.

Figure 1 illustrates the movement of the fuels. Hydrazine and UDMH are shipped from the manufacturer to the blending facility by rail to make A-50; MMH is trucked to both launch sites and A-50 is trucked to one launch site and transported by rail to the other launch site. Table 4 is a theoretical annual transportation plan to accomodate fuel usage plus a two year stockpile of A-50 and a four year stockpile of MMH. Truck capacity is assumed at 40,000 pounds; rail car capacity is 55,000 pounds for AH and MMH and 68,000 pounds for UDMH and A-50 respectively. This gives us a total of 182,470 miles of rail car transportation and 216,170 miles of truck transportation for the next ten years. Applying the derived accident rates for rail cars and trucks we predict 0.21 truck accidents and 0.68 rail car accidents for a total of slightly less than one accident predicted for the ten year period (Table 5). The ten year prediction does not change appreciably by the more conservative treatment of averaging the accident data --0.48 truck accidents and 0.55 rail car accidents, for a total of little more than one. Because of the larger capacity of the rail car as compared to the truck both the truck accident and rail car accident per million pound miles (UDMH) are about equal within the accuracy of this study.

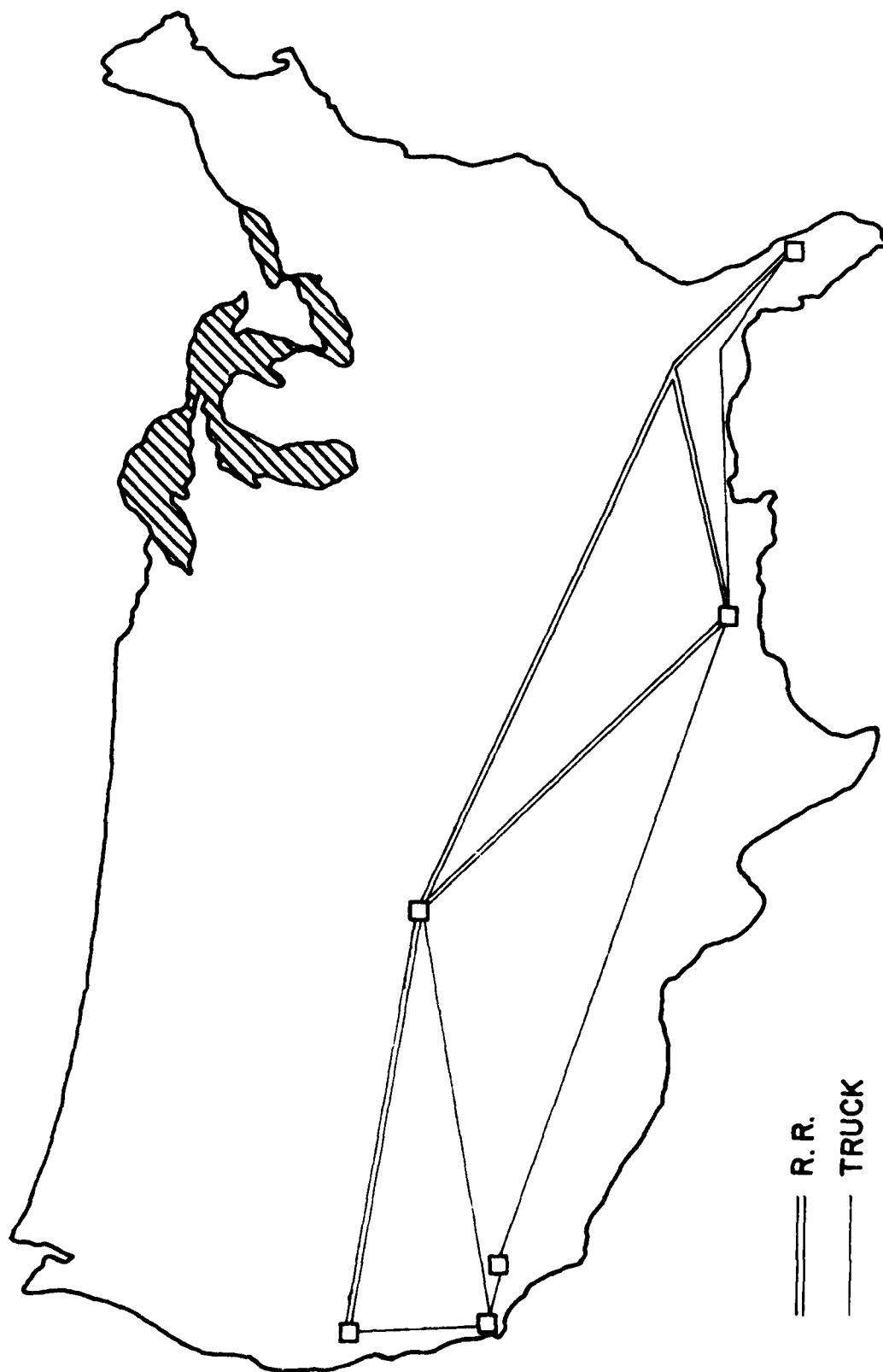


Figure 1. Transportation Mode

TABLE 3. 10 YEAR LAUNCH VEHICLE FUEL USAGE FORECAST (POUND X 10<sup>-3</sup>)

FUEL	FISCAL YEAR									
	79	80	81	82	83	84	85	86	87	88
<u>UDMH/AH</u>										
West Coast Total	898	877	864	434	548	430	120	-		
VAFB	(522)	(488)	(488)	(244)	(360)	(240)	(120)	-		
ALRC	(376)	(378)	(376)	(190)	(188)	(190)	-	-		
East Coast	494	0	494	494	247	-	-	-		
TOTAL	<u>1392</u>	<u>866</u>	<u>1358</u>	<u>928</u>	<u>795</u>	<u>430</u>	<u>120</u>			
Stockpile Required (2 yr)	2258	2224	2286	1723	1225	550	120			
<u>MMH</u>										
West Coast	-	-	-	-	38	94	162	218	286	243
East Coast	328	179	132	195	260	390	442	468	442	442
TOTAL	<u>328</u>	<u>179</u>	<u>132</u>	<u>195</u>	<u>298</u>	<u>484</u>	<u>504</u>	<u>686</u>	<u>728</u>	<u>685</u>
Stockpiled Required (4 yr)	834	804	1109	1481	1972	2402	2603	2746	2737	2712

TABLE 4. 10 YEAR HYDRAZINE FUEL TRANSPORTATION PLAN

	1979	1980	1981	1982	1983	1984	1985	1986	1987	1988	Total
<u>RAILCAR TRIPS</u>											
Lake Charles to RMA	8	14	6	4	0	0	0	0	0	0	
(1350 mi)											
RMA to ALRC	10	13	6	1	0	0	0	0	0	0	
(1160 mi)											
RMA to ETR	0	3	0	0	0	0	0	0	0	0	
(2300 mi)											
RMA to ETR	10	0	10	6	3	0	0	0	0	0	
(2300 mi)											
Lake Charles to ETR	5	0	0	0	0	0	0	0	0	0	
(1060 mi)											
Total Railcar Miles	50,700	57,080	47,510	27,110	6,900	0	0	0	0	0	182,470
<u>TRUCK TRIPS</u>											
RMA to WTR	12	13	9	4	9	0	0	0	0	0	
(1180 mi)											
ALRC to WTR	0	0	0	0	0	3	0	0	0	0	
(300 mi)											
Lake Charles to AFFTC	0	0	8	5	1	2	5	6	7	6	
(1700 mi)											
AFFTC to WTR	0	0	8	5	1	2	5	6	7	6	
(240 mi)											
Lake Charles to ETR	0	0	7	13	15	19	11	12	11	11	
Total Truck Miles	14,160	15,340	32,090	25,470	25,310	20,930	19,050	21,840	22,930	19,050	216,170

TABLE 5. PREDICTED ACCIDENT RATE

	<u>TREND</u>	<u>AVERAGE</u>
A. RAIL CAR ACCIDENT PER MILLION CAR MILES	3.70	2.99
B. TRUCK ACCIDENTS PER MILLION VEHICLE MILES	0.95	2.24
C. PREDICTED TEN YEAR HYDRAZINE FUEL ACCIDENTS		
1. RAIL CAR	.68	.55
2. TRUCK	<u>.21</u>	<u>.48</u>
TOTAL	.89	1.03
D. RAIL CAR ACCIDENT PER MILLION UDMH POUND MILES X 10 <sup>5</sup>	5.44	4.40
E. TRUCK ACCIDENTS PER MILLION UDMH POUND MILES X 10 <sup>-5</sup>	2.38	5.60

PAPER NO. 4

## BIOLOGICAL EFFECTS OF HYDRAZINE

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The biological impact of hydrazine fuels on the ecosystem in which it is used is of ultimate importance to the Air Force since this level of impact is directly coupled to the socioeconomic, medical and legal constraints on the use of it as a fuel. The purpose of this paper is to summarize the recent work done by this laboratory in the area of biological effects. The hydrazine work was done under contract and by in-house investigators. Only the contracted work is described in this presentation, and the reported information was extracted from the most recent annual progress report (references 1, 2, and 3).

The contract work was done at the University of California, Irvine Campus (UCI). The work considered algal systems as indicators of ecological stress. Both freshwater and seawater algal systems were studied. The Berkley Campus (UCB) is performing bioassay work on fish and aufwuchs in an effort to define the effects of potential environmental contamination on fish.

### ALGAL STUDIES

As just mentioned, the University of California, Irvine Campus studied both freshwater and marine algae. The same general proce-

dures were followed in both cases, in that algal systems were systematically exposed to various concentrations of hydrazine in a batch type exposure of a closed algal system.

University of California, Irvine, research objectives for the past year were directed toward the establishment of dose/concentration responses of unicellular green algae to hydrazine, unsymmetrical dimethylhydrazine (UDMH), and monomethylhydrazine (MMH). Dose responses were determined for two algal species using the Standard Algal Bioassay procedure. Both freshwater and marine bioassays were conducted to simulate a range of aquatic ecosystems, such as oligotrophic lakes, eutrophic lakes, lakes of intermediate trophic status, estuaries and the open sea. The overall goals were to provide information for environmental impact statements and determine threshold limits under which the Air Force can operate within the National Environmental Policy Act. The specific objectives were:

1. Determine "no effect" or safe concentration (SC) for the compounds under the various test conditions.
2. Determining EC<sub>50</sub> for the compounds under various test conditions.

The "no effect" or safe concentration (SC) were determined by using a t-test to compare mean growth in the control flasks with mean growth for each concentration of test compound. The SC is the highest concentration of test compound which causes no statis-

tically significant difference in growth (at the 95 percent confidence level) when compared with the control flasks without test compound added.

Effective concentrations were determined graphically by plotting percent algal growth as a function of the initial concentration of test compound. The  $EC_{50}$  is that concentration which causes a 50 percent reduction in growth when compared with the controls without chemical added. The total cell number was used as the algal growth index. This paper provides detailed results from the work conducted during 1977/78 and presents a comprehensive summary of all the testing and results of hydrazine toxicities obtained in the previous two years under the conditions presented below in Table 1 and Table 2. With respect to these Tables, the nutrient levels for the experiments are equivalent to the following natural conditions:

Freshwater: The ranges used correspond to oligotrophic (10 percent SAAM nutrients), intermediate (33 percent SAAM nutrients) and eutrophic (100 percent SAAM nutrients).

Seawater: The seawater experiments were conducted over a range of salinity and nutrient levels. At a salinity of 33 ppt, the lower nutrient level (10 percent SAAM nutrients) is equivalent to conditions encountered near sewage outfalls or off the mouths of estuaries where nutrient-rich drainage from agriculture occurs. The experiments at lower salinities (16 ppt, 24 ppt) and the same two levels of nutrients (10 percent SAAM, 33 percent SAAM) simulate conditions found in estuaries of differing nutrients status.

TABLE 1.

COMPOUNDS TESTED AND TEST CONDITIONS OF 1976/77 BIOASSAYS

COMPOUND	TEST CONDITIONS	
	Type of Water	Nutrient Level
Hydrazine	Freshwater	10% SAAM nutrients
	Freshwater	33% SAAM nutrients
	Freshwater	100% SAAM nutrients
UDMH	Freshwater	10% SAAM nutrients
	Freshwater	33% SAAM nutrients
	Freshwater	100% SAAM nutrients
MMH	Marine, 35 ppt salinity	33% SAAM nutrients
	Marine, 35 ppt salinity	33% SAAM nutrients

TABLE 2.

COMPOUNDS TESTED AND TEST CONDITIONS OF 1977/78 BIOASSAYS

COMPOUND	TEST CONDITIONS	
	Type of Water	Nutrient Level
Hydrazine	Marine, 16 ppt salinity	10% SAAM nutrients
	Marine, 16 ppt salinity	33% SAAM nutrients
	Marine, 24 ppt salinity	10% SAAM nutrients
UDMH	Marine, 24 ppt salinity	33% SAAM nutrients
	Marine, 35 ppt salinity	10% SAAM nutrients
	Marine, 24 ppt salinity	10% SAAM nutrients
	Marine, 16 ppt salinity	33% SAAM nutrients
	Marine, 16 ppt salinity	10% SAAM nutrients
	Marine, 16 ppt salinity	33% SAAM nutrients
MMH	Freshwater	10% SAAM nutrients
	Freshwater	33% SAAM nutrients
	Freshwater	100% SAAM nutrients
	Marine, 35 ppt salinity	10% SAAM nutrients
	Marine, 35 ppt salinity	33% SAAM nutrients
	Marine, 24 ppt salinity	10% SAAM nutrients
	Marine, 24 ppt salinity	33% SAAM nutrients
	Marine, 16 ppt salinity	10% SAAM nutrients
	Marine, 16 ppt salinity	33% SAAM nutrients

The environmental effects of the three hydrazine compounds as determined under the different aquatic conditions of salinity and nutrient concentrations have been outlined. These results are summarized below for each of the compounds tested. The number of algal cells grown as well as the total algal cell volumes have been used as the two measures of potential effects on the test species. The concentrations of hydrazine compounds that have a potential effect have been determined both on the basis of Safe Concentrations (SC) and Median Effective Concentration (EC<sub>50</sub>) as discussed above.

#### Environmental Effect of Hydrazine

The hydrazine concentrations were prepared by successive dilution. As the detection limit for hydrazine (0.005 ul/l) in the method used for analysis is greater than most of the initial concentrations used for experiments, direct verification of the amount present was not possible. Once the experiments had begun, hydrazine could not be detected in any of the flasks after two days. Flasks were seeded with Dunaliella tertiolecta of initial cell concentration  $1 \times 10^6$  cells/l and algal growth was monitored on days 6, 8, and 10.

Algal bioassays were conducted utilizing five replicates for each of the following initial hydrazine concentrations; 0.000, 0.0001, 0.0005, 0.0010, 0.0030, 0.0050, and 0.0100 ul/l of ASW medium.

Using the results obtained on growth day 6 as a representative indication there is no significant difference between the results

obtained using cell number or cell volume as the response parameter. The Safe Concentration ranged from 0.001 ul/l under oligotrophic freshwater conditions to 0.0001 ul/l under oligotrophic brackish conditions. The corresponding EC<sub>50</sub> range is from 0.03 ul/l to 0.0004 ul/l.

There is little difference between the SC and EC<sub>50</sub> values obtained at the various brackish and seawater salinity levels. This indicates that the cause of the range is not salinity variations or amount of nutrients present. Instead, the observed difference in SC and EC<sub>50</sub> values indicate that there is a very significant difference in sensitivity between the two alga used under freshwater and brackish/seawater conditions, respectively.

The saltwater alga Dunaliella tertiolecta is affected by concentrations of hydrazine which are one order of magnitude lower than the concentration required to affect the growth of Selenastrum capricornutum. Based on these results additional work is being conducted evaluating a number of different test alga to determine the range of sensitivity that can be expected in natural algal populations.

#### Environmental Effect of Monomethylhydrazine

The present studies examined the responses of freshwater alga, Selenastrum capricornutum, and the marine flagellate, Dunaliella tertiolecta. In all cases, five controls without MMH and five replicates flasks for each concentration of MMH were seeded to an

initial concentration of  $1 \times 10^6$  cells per liter. Algal growth (both cells number and total cell volume) and MMH concentrations were measured at intervals for at least 10 days and in some cases as long as 31 days.

The bioassays were conducted using initial MMH concentrations of 0.20, 0.40, 0.60, 0.80, 1.00, and 2.00 ul MMH/l in the brackish/seawater tests.

The results show that the SC based on cell volumes measured at Day 6 range from 0.2 ul MMH/l in saltwater. The corresponding EC<sub>50</sub> values from 0.3 ul MMH/l to 1.2 ul MMH/l.

Examination of Coulter Counter data for the freshwater assays with Selenastrum capricornutum as the test organism showed a progressive increase in mean algal cell volume as the MMH concentration increased. This increase in cell size at the higher MMH concentration seems to indicate that MMH does not kill algal cells but inhibits cell division because of interference with some metabolic pathway. Therefore, the cells continue to exist for some time after MMH concentration drops to a level which, initially, would not be growth inhibiting. Once the metabolic interference is overcome, the cells begin to divide very rapidly so that the algal culture consists of new, slightly smaller cells. Further evidence of the growth inhibiting effect, rather than lethality of MMH is the fact that all flasks which had an initial 1.0 ul/l concentration grew well after 30 to 40 days.

### Environmental Effects of Unsymmetrical Dimethylhydrazine

Algal assays were conducted using a range of UDMH concentrations from 0.0 to 3.0 ul/l. Using the values of Day 6, the results show that the SC, based on total cell volume as the key parameter, range from 5.0 ul/l in seawater. The Safe Concentration, determined by evaluating cell numbers rather than total cell volumes, are lower for freshwater conditions. This indicates that as with MMH, UDMH inhibits cell division.

### Comparison of the Safe Concentration and Fifty Percent Effective Concentration for Hydrazine Compounds

The results of all experiments can be summarized to show the relative toxicity of the three hydrazine compounds under the range of water qualities and organisms tested. The summary results in Table 3 show that hydrazine is the most toxic of the three compounds under both freshwater and seawater assay conditions. The SC for UDMH was measured after six days of growth. Both SC and EC<sub>50</sub> are higher under seawater conditions than under freshwater conditions for hydrazine and MMH with the reverse for UDMH. This difference appears to be due to the different sensitivity of the two test algae used in freshwater and seawater.

Results in Table 3 are initial concentrations of compound in ul/l which result in no effect (Safe Concentration) and in a 50 percent growth reduction on Day 6 on the basis of total cell volume biomass. One of the explanations for the apparant higher toxicity

(lower Safe Concentration and Fifty Percent Effective Concentration) for hydrazine compared with MMH and UDMH is the much higher stability of the former. Thus, in the terms of potential impact on the aquatic environment, the use of MMH and UDMH is recommended as being preferable to hydrazine, based on the results obtained in this investigation.

TABLE 3. TOXICITY OF HYDRAZINE COMPOUNDS TO ALGAE

TYPE OF WATER TEST ORGANISM	<u>Hydrazine</u>		<u>MMH</u>		<u>UDMH</u>	
	SC	EC <sub>50</sub>	SC	EC <sub>50</sub>	SC	EC <sub>50</sub>
Oligotrophic freshwater <i>S. capricornutum</i>	0.0001	1.030	0.2	0.5	2.0	5.0
Oligotrophic seawater <i>C. tertiolecta</i>	1.0005	0.0008	0.8	1.1	0.1	2.3

#### FISH STUDIES

Studies were conducted to assess the toxicity of the hydrazines (1-Methylhydrazine (MMH), 1, 1-dimethylhydrazine (UDMH)) to plant and animal species indigenous to the Central San Francisco Bay. Aufwuchs and 3-spine sticklebacks were exposed to MMH and UDMH in "spill" studies conducted in analog tanks and in range finding laboratory jar test. "Spill" studies and jar test pertaining to hydrazine toxicity, reported here, includes a 14 day continuous flow analog study of aufwuchs and a 96 hour continuous flow analog bioassay. Continuous-flow studies with UDMH and MMH are planned for the near future.

### UDMH Studies

Jar Test. Based on the results of a range-finding study, a static acute 96 hour bioassay was conducted in duplicate for UDMH concentrations of 0, 0.32, 0.56, 1.0, and 3.2 mg/l. Ten stickleback were placed in a 20 liter jar containing 18 liters of toxicants solution for each duplicate concentration of UDMH. The UDMH solutions were renewed every 24 hours because of the rapid UDMH decay rate in bay water. The jars were covered with aluminum foil and were greatly aerated. Throughout the bioassay the pH of the dilutions averaged 7.8 and the dissolved oxygen (DO) was in the range of 5.4 - 6.8 mg/l; both acceptable values for this species.

The results indicate that short-term mortalities occurred in the range of initial UDMH concentrations between 1.0 and 3.2 mg/l. The mean 96 hour LC 50 for the duplicate bioassays was 1.63 mg/l, and satisfactory replication was achieved.

Spill Studies. A study was performed at initial concentrations of 0.0, 0.1, and 3.2 mg UDMH/l in duplicate and at concentrations of 10.0 and 19.3 mg UDMH/l without duplication.

Aufwuchs growths were developed during an 11 day period in the analog tanks in which each received a continuous-flow of 4.8 l/min of bay water. Upon introduction of sticklebacks (10 per tank) and UDMH, the bay water pumps were shut down and the analog tanks operated in a static mode for the ensuing 96 hour bioassay period. Aufwuchs were removed from the tanks after 24 hour exposure to

UDMH. During the bioassay the water temperature was in the range of 13-19°C, the pH was approximately 7.8 and the chlorosity was 17.6 g/l.

The data indicated that all fish died within 96 hours in the tanks containing initial UDMH concentrations of 10 mg/l and 19.3 mg/l. Significant fish mortality occurred in the tank containing an initial UDMH concentration of 10.0 mg/l even after all measurable UDMH had disappeared from solution. Examination of UDMH concentration in the system by withdrawal of samples from a depth of 20 cm showed that UDMH had virtually all disappeared from solution within 7 hours of its introduction.

The concentrations of UDMH after 1 hour in several of the analog tanks were higher than would be expected if complete mixing had occurred. This demonstrated that the UDMH was stratifying on the surface. Such stratification has important implications for the environment. In a real spill the organisms staying near the surface would be more seriously affected than bottom dwellers. Based on initial UDMH concentrations, the 96 hour no-effect level of survival was between 3.2 and 10 mg/l.

The effect of the spill on aufwuchs was determined. There was a significant reduction of photosynthesis index (PIs) for aufwuchs in the tanks containing initial UDMH concentrations of 10 and 19.3 mg/l. This indicates that UDMH is toxic to aufwuchs at these levels. There was also a noticeable reduction in the organic matter content of aufwuchs subjected to these two initial UDMH

concentrations but it is not possible to conclude that this reduction is caused by the toxicant since the values are within the normally expected range of values. The data indicate that the no-effect level for aufwuchs is between an initial level of 3.2 to 10.0 mg UDMH/l.

#### MMH Studies

Jar Test. A static bioassay was conducted to determine the 96 hour LC 50 of MMH to the 3-spine stickleback. Based on the findings of the preliminary study, the range of initial toxicant concentrations investigated was 0 to 3.2 mg MMH/l. Six initial concentrations, 0, 0.32, 0.56, 1.0, and 3.2 mg/l, were studied in duplicate in 20 liter capacity jugs, each containing 16 liters of Bay water. In one set of jugs, 10 fish were exposed to each concentration. Because of the previously determined high rate of MMH loss (65 percent in 6.5 hours), the MMH solutions were renewed daily. The jugs were covered with aluminum foil and gently aerated with house air. Aeration was sufficient to maintain the minimum DO of 6 mg/l throughout the bioassay. Water temperature was in the range of 19-20°C, the pH was 8.95, and the chlorosity was 14.9 g/l.

Results show that no fish survived the first day of exposure in the jar containing an initial MMH concentration of 3.2 mg/l; all of the fish were dead within 6 hours. In the jar containing an initial MMH level of 1.0 mg/l there were no survivors after 48 hours of exposure.

The LC 50's of the duplicate samples, expressed as initial MMH concentrations were 1.4 mg/l and 1.9 mg/l at 24 hours, 0.60 mg/l and 0.46 mg/l at 48 hours, and 0.32 and 0.40 mg/l at 96 hours. During each 24 hour period between MMH renewals, MMH disappeared rapidly and was completely gone before the subsequent 24 hour renewal. In view of the rapid decay of MMH, there is no doubt that in a continuous-flow bioassay where steady levels of MMH could be maintained, the LC 50 values would be considerably lower than those indicated above.

Spill Study. A study of MMH toxicity of stickleback and aufwuchs was conducted following the general procedures described earlier for the UDMH study. Growth units were examined 24 hours after MMH addition to determine the effect of metabolic response, chlorophyll a content and biomass. Initial MMH concentrations of 0, 0.56, 1.0, and 3.2 mg/l were used in duplicate sets of analog tanks. The possibility of toxicity caused by MMH degradation to ammonia was assessed by routine monitoring of ammonia levels.

Results of fish survival show that significant mortality occurred only within the initial 24 hour period following MMH addition and only in the tanks containing an initial MMH concentration of 3.2 mg/l. The no-effect level to stickleback for a spill situation is therefore between 1.0-3.2 mg MMH/l. As would be expected, MMH toxicity to sticklebacks was less in the analog tank spill situation than in the jar test where the solutions were renewed daily.

#### Hydrazine Studies

A 96 hour Bioassay. A study was conducted to determine the LC 50 of hydrazine to the stickleback, the bay mussels (Mytilus Edulis), and the mud flat crab (Hemigrapsus oregonensis). In addition, the experiment attempted to determine changes in the metabolic rate (productivity) of the aufwuchs community.

Approximately 100 mussels and 100 crabs were collected; the mussels were scrubbed clean of epiphytic growth and pooled into 8 sets of 10 mussels each. Each set was placed in a 50 cm x 15 cm, 4.0 mm mesh Nytex bag and suspended in Bay water 50 cm below the surface of the holding tank. The crabs were also pooled into 8 sets of 10 crabs each and placed into cylindrical fish cages. The 8 cages were covered with aluminum foil and suspended 28 cm below the water surface in a holding tank. The two types of organisms were acclimated for 9 days. Additionally, sticklebacks were divided into 8 sets of 30 fish each, placed in fish cages and acclimated for 12 days in a holding tank.

Eight aufwuchs racks, each containing 30 substrates, were suspended 50 cm below water surface in a holding tank. Aufwuchs growth developed during a period of 12 days prior to exposure to hydrazine.

All 3 test organisms and the aufwuchs communities were maintained in Bay water at a flow rate of 4.0 l/min. The nominal hydraulic residence time for an analog tank at this flow rate was estimated to be about 17.4 hours.

The organisms and the aufwuchs community were exposed in duplicate to hydrazine concentrations of 0 (control), 1.0, 1.8, and 3.2 mg/l.

Hydrazine was pumped at a rate of 1.0 ml/min by Buchler polystaltic pumps into the seawater inflow pipes of each of the 6 tanks. The tanks were equilibrated for 120 hours prior to the commencement of the experiment.

At the start of the experiment the fish, mussels, and crabs were placed in each of the 8 analog tanks. The organisms were checked at 24 hour intervals for mortality; dead animals were removed immediately. Animals were considered dead when they no longer responded to probing.

The data show that the high mortality of both fish and crabs occurred at the highest hydrazine concentration (5.7 mg/l). The average percent mortality at 96 hours at 5.7 mg hydrazine/l was 55 percent; 26 percent of the surviving fish displayed "stressed" behavior, such as erratic swimming, disorientation, and increase respiration rates. All of the crabs were dead in both duplicates of the highest hydrazine concentrations (5.7 mg/l). The crabs appear to be more sensitive to hydrazine than the sticklebacks since a mortality of 80-100 percent occurred after 48 hours of exposure. The mussels were the most tolerant of the organisms tested. Only a 5 percent mortality occurred at one of the highest hydrazine concentrations. The experiment appeared to be too short to elicit significant mortalities of this organism.

The 96 hour LC 50's for both stickleback and crabs were calculated by the best fit line from the mortality results plotted on logarithmic-probability paper. The 96 hour LC 50's for stickleback and crab were 5.4 mg/l and 3.6 mg/l, respectively.

The amount of growth on the aufwuchs substrates was 8-9 mg (in the controls) and ranged downwards to 3-4 mg on the aufwuchs exposed to various concentrations of hydrazine. The data show a severe toxic effect after 48 hours and a more pronounced effect after 96 hours on aufwuchs exposed to hydrazine concentrations examined. The aufwuchs exposed to hydrazine had a sharply reduced biomass, chlorophyll a, b and c, gross photosynthesis, and PI indicator compared to the control aufwuchs. The gross photosynthesis, a sensitive indicator of toxicity, show 96 hour levels at the 2.2 mg hydrazine/l level (the lowest level tested) that are about 10 percent of the control. In the higher levels of 2.9 and 5.7 mg/l of hydrazine tested there was over 95 percent reduction in these parameters compared with the control aufwuchs. Pheophytin a content was negligible or absent in all aufwuchs including the controls. These results indicate that the aufwuchs are much more sensitive indicators of hydrazine toxicity than stickleback.

A 14-Day Continuous Flow Bioassay. A 14-day continuous flow study was conducted on the same species, obtained from the same sources, studied in the preceeding 96 hour bioassay.

A aufwuchs growth rack containing substrates was placed in each of the 8 analog tanks at the start of the experiment to observe the effect of hydrazine on aufwuchs development. This was different from the previous 96 hour study where the aufwuchs were developed before being exposed to hydrazine. The aufwuchs were examined after 7 days (168 hours) and after 14 days (336 hours) of exposure to hydrazine.

The target hydrazine concentrations were 0 (control), 0.75, 1.35, and 2.4 mg hydrazine/l. Stock solutions of hydrazine were pumped into the analog tanks for a 24 hour period of equilibration before initiating the study. Test organisms were observed each day for mortality, and dead animals were immediately removed.

Bioassay results showed that the mortality of the stickleback and crab increased with increasing hydrazine concentrations. At the highest hydrazine concentrations (1.72 mg/l) the average mortality was 80 percent. "Stressed" behavior, such as disoriented swimming, increased respiration rate and lying sideways, was observed in 60-85 percent and 25-38 percent of the surviving fish at the highest (1.72 mg/l) and the next highest (0.98 mg/l) hydrazine concentrations, respectively.

At the highest hydrazine concentration (1.72 mg/l) all crabs were dead by 336 hours (14 days). The 336 hour LC 50's were calculated for stickleback and crab. The 336 hours (14 days) LC 50 for stickleback was 1.07 mg/l; the value for the crab was estimated to be 0.56 mg/l. For the mussels, there was no toxic responses in the range of hydrazine concentrations tested.

In all aufwuchs exposed to hydrazine, growth, as assessed by dry weight, was severely reduced over that observed in the control. Neither the control aufwuchs nor the aufwuchs exposed to the lowest hydrazine concentrations (0.53 mg/l and 0.98 mg/l) exhibited any increase in dry weight between the 7 day and 14 day measurements. Perhaps these results are an indication that the aufwuchs

exposed to the two lowest hydrazine concentrations reached a steady state level of growth which could be maintained in the presence of the given hydrazine concentration. Further experiments are needed to justify this contention.

The organic matter content of the growth that occurred in all aufwuchs was similar and in the range of 26-50 percent of the dry weight. Because of the extremely low dry weights of aufwuchs growth in this study the amounts of the chlorophyll a, b and c, were also extremely small and pheophytin was not detected. These low values may have contributed to the somewhat inconsistent responses of the concentrations of the various chlorophylls to different hydrazine concentrations. In the chlorophyll a data there are evidence of a consistent response to various levels of hydrazine. Both at 168 hours and 336 hours the aufwuchs exposed to increasing levels of hydrazine between 0 and 1.72 mg/l contained decreasing amounts of chlorophyll a. Results of photosynthetic rate measurements show distinct evidence of the toxicity of hydrazine as indicated by both gross photosynthesis (mg O<sub>2</sub>/aufwuchs substrate-hour) and photosynthetic index based on dry weight (mg O<sub>2</sub>/dry-weight-hour). In both of these expressions of photosynthetic activity there is a suggestion that at each of the lower levels of hydrazine (0.53 and 0.98 mg/l) a recovery from the toxic effects of hydrazine was evident. Further experiments with more significant aufwuchs growths and for a longer duration than 14 days are necessary to determine whether these data are truly representative of the situation. The photosynthetic index measurements based on

chlorophyll a are not as consistent as those based on dry weight, possibly because of the difficulty in accurately measuring the low amounts of chlorophyll. However, these data show clearly that the aufwuchs exposed to 1.72 mg hydrazine/l had a severely suppressed PI value based on chlorophyll a.

While the aufwuchs data are somewhat tenuous because of the very small amount of growth obtained, it is quite evident that hydrazine is far more toxic to aufwuchs than to sticklebacks. Evidence shows that aufwuchs exposed to 0.53 and 0.98 mg hydrazine/l may become adapted to these levels after an extended period of time. It will be necessary to repeat these continuous-flow studies using much heavier aufwuchs growths at lower hydrazine concentrations range for a longer period of time than 14 days.

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TOXICITY OF HYDRAZINE TO SELECTED BACTERIA

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1. INTRODUCTION

The increased use and geographical distribution of hydrazine fuel in the United States has stimulated interest in the environment toxicology of hydrazine. Various efforts are underway to determine the fate and effect of hydrazine in the environment. These toxicological and metabolic studies of hydrazine deal with a broad spectrum of biological entities ranging from common bacteria to man. The Civil Engineering Department of Oregon State University is currently conducting a fate and effect study of hydrazine using a variety of bacteria. The bacteria employed have been chosen as representative of the dominant populations found in soil, surface waters and in wastewater treatment facilities. The Oregon State study was proposed to achieve the following objectives:

1. To evaluate the biological degradation of hydrazine under aerobic and anaerobic conditions with emphasis on possible nitrification-denitrification pathways.

2. To evaluate the toxicity of hydrazine to a variety of heterotrophic and autotrophic bacteria.

3. To determine the fate of hydrazine entering biological systems.

4. To develop a model of the biological degradation of hydrazine in freshwater aquatic environment.

The information presented is a preliminary report on progress and findings to date. Since the research is continuing, data reported here may be interpreted differently in the light of future developments.

## II. PROCEDURE AND RESULTS

### A. PRELIMINARY HYDRAZINE DEGRADATION STUDIES

Based on information supplied by the Civil and Environmental Engineering Development Office (CEEDO), degradation studies of hydrazine in various solutions of interest were accomplished. Hydrazine concentrations ranged from 5 to 20 mg/l as hydrazine. A typical degradation series is shown in Figure 1. From these studies it was determined that:

1. Hydrazine degradation was extremely slow in all solutions of interest that were devoid of living organisms.

2. Hydrazine degradation was significant when bacteria were present which suggested active metabolism.

### B. APPROACH TO THE EFFECT PORTION OF THE STUDY

Four bacteria populations were selected for the effect portion of this study and they are as follows:

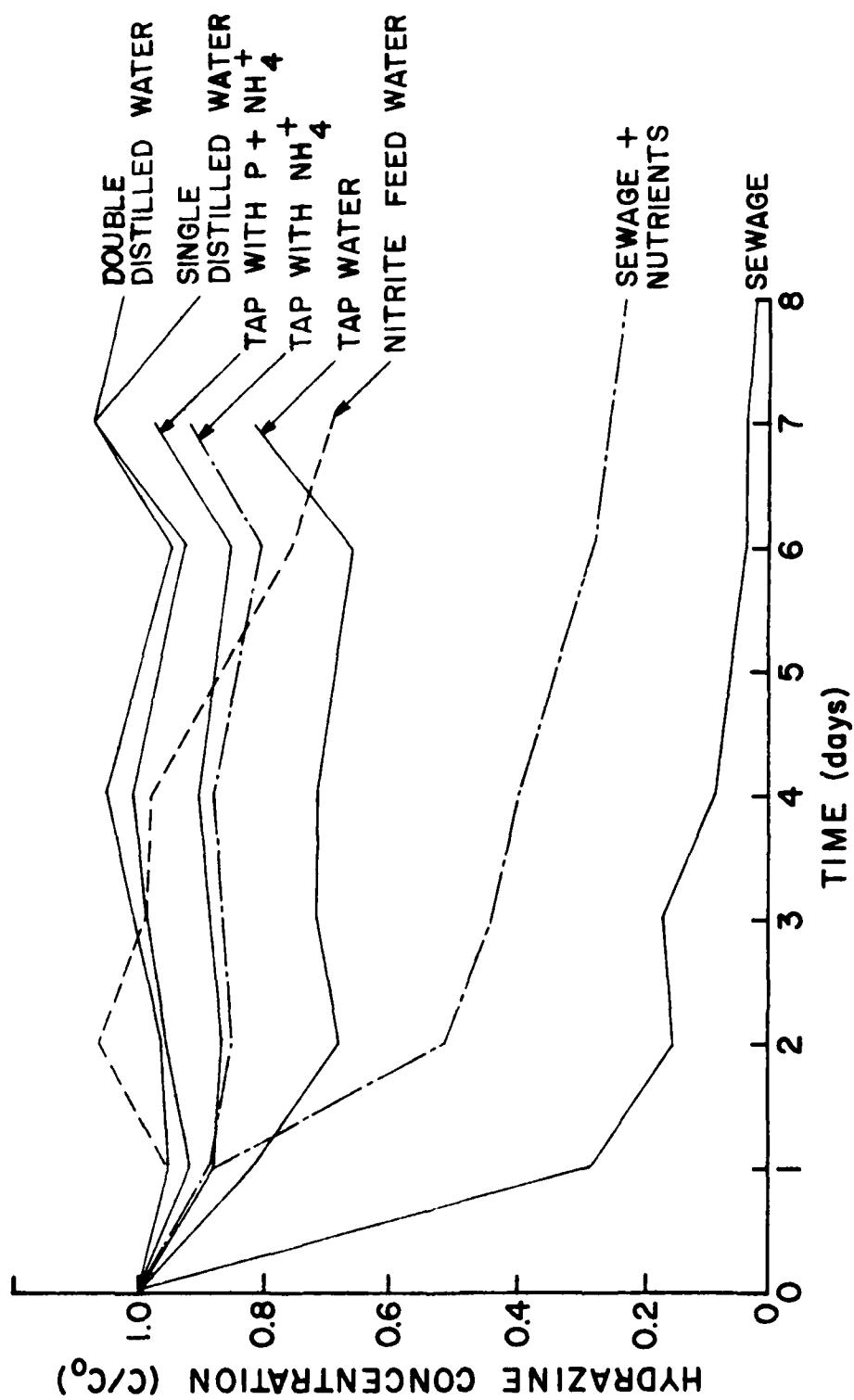


Figure 1. Hydrazine Concentration  $C/C_0$  versus Time

1. Nitrobacter. Slow growing bacteria converting  $\text{NO}_2$  to  $\text{NO}_3$  for energy and using  $\text{CO}_2$  as a carbon source.
2. Nitrosomonas-Nitrobacter. Slow growing bacteria converting  $\text{NH}_4$  to  $\text{NO}_2$  (Nitrosomonas) and  $\text{NO}_2$  to  $\text{NO}_3$  using  $\text{CO}_2$  for cellular carbon.
3. Denitrifying bacteria. Bacteria capable of converting  $\text{NO}_3$  to  $\text{NO}_2$  and then to  $\text{N}_2$  gas. An organic such as methanol is used as a carbon source.
4. Anaerobic bacteria. A mixed population of acid formers and methane formers capable of converting a wide range of complex wastes to  $\text{CO}_2$ ,  $\text{CH}_4$  and  $\text{H}_2\text{O}$ .

It is worthwhile to examine the spectra of the nitrogen oxidation scheme in order to see the reported hydrazine degradation pathways and to imagine possible metabolic involvement of these four groups of bacteria. Figure 2 shows this scheme, compounds of interest and the four populations involved in our study.

#### C. NITROBACTER BIOASSAY STUDIES

As seen in Figure 2, the substrate metabolizing pathway of Nitrobacter is far removed from the expected oxidation changes for hydrazine. Nitrobacter was selected not because hydrazine might serve as a substrate but because of the uniqueness of Nitrobacter as a bioassay tool to assess toxicity. The Nitrobacter bioassay as used in our work was developed by Williamson (reference 16) to take advantage of four features characteristic of this bacteria:

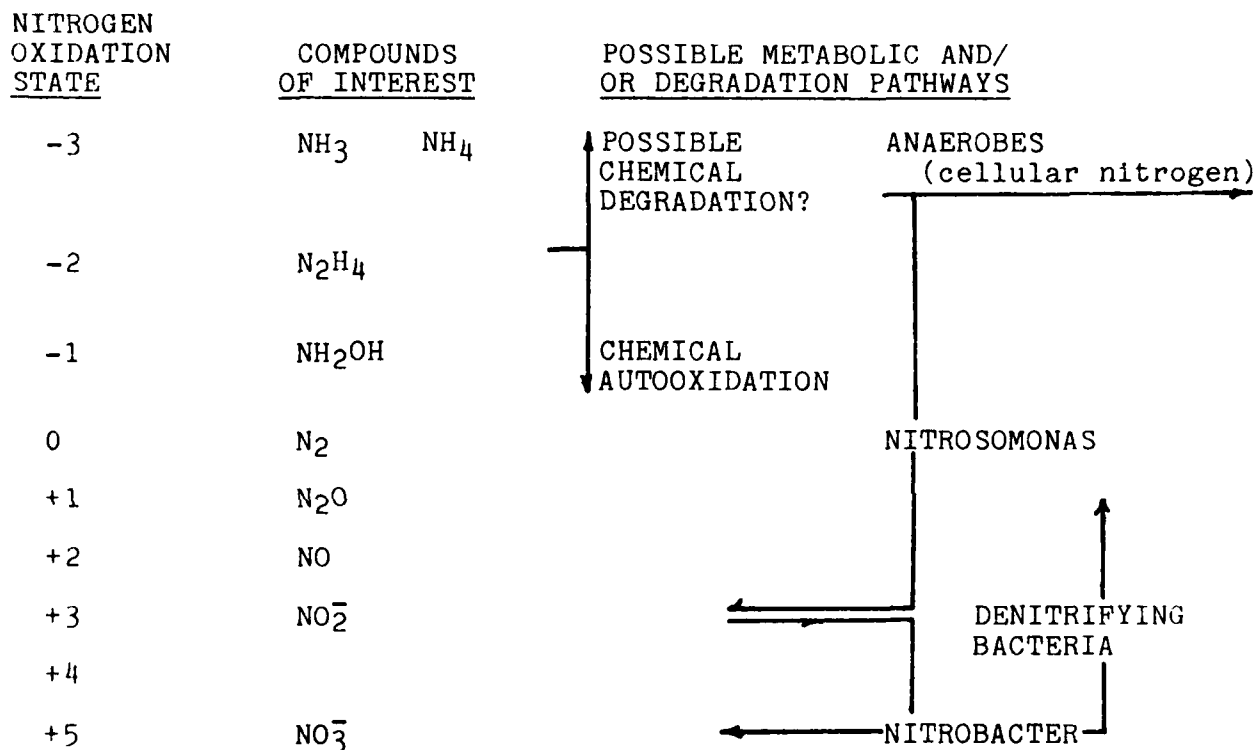


Figure 2. Bioassay Populations, Nitrogen Compounds of Interest and the Oxidation States of Nitrogen

1. Nitrobacter is ubiquitous in the aquatic environment.
2. It offers a simple quantification of removal rate by monitoring nitrite depletion.
3. The slow growth rate of Nitrobacter offers the use of batch-fed tests with minimal incorporation of substrate into cellular material.
4. Nitrobacter is as sensitive or more sensitive to most toxicants as other heterotrophic organisms and can serve as an indication species.

The Nitrobacter was grown in a short downflow column full of small (1 mm diameter) bouyant polyethylene beads that served to trap the bacteria and to distribute the flow evenly. The substrate consisted of 20 mg/l of nitrogen as sodium nitrite, 1 mg/l of phosphorus as potassium phosphate dibasic, all in tap water with an unadjusted pH of 7. The feed was mixed with pure oxygen to ensure a maximum oxygen concentration as the feed entered the column. The bacteria were harvested from the bottom of the column and the beads were returned to the top of the column. The bacteria were then concentrated in a freshly prepared nitrite solution (same concentration as used in bioassay) before being measured and introduced into a 250 ml Erlenmeyer flask and placed on a 20°C water-shaker bath. After a short equilibrium period, the bioassay was initiated and the nitrite concentrations measured every 30 minutes (reference 4, Sec 134) until the

controls removed all but about 2-3 mg/l nitrite, usually in about 2-3 hours. At this point, the bacteria were filtered out of solution with a glass fiber filter and the biomass determined (total suspended solids, TSS). Nitrate and ammonia determinations were made using Orion specific ion probes. Normally, killed bacteria were also carried through the bioassay (killed by heating above 90°C) to determine the amount of nitrite converted to nitrate by cellular debris. Little or no such conversion was observed.

Toxicity was defined by comparing the nitrite removed in those units receiving the hydrazine with the control unit. Removal was expressed as a percent of that for the control depletion rate and calculated as milligrams substrate removed per milligram of TSS per day. Typical results are shown in Table 1 in terms of hydrazine concentration and the hydrazine dose employed per milligram of cells used (TSS). The maximum substrate removal rates were determined for all controls which allowed comparison of bioassays from one day to the next as the bacteria culture changed with age.

The results as expressed in Table 1 indicate that if toxicity is defined as 50 percent inhibition of the substrate removal rate, the toxic concentration of hydrazine for Nitrobacter is in the 20 to 30 mg/l range (50 to 150 ug  $N_2H_4$ /mg TSS) with total inhibition above about 100 mg/l.

An attempt was made to account for the nitrogen balance changes in each bioassay but the results were disappointing. Differences due to analytical methods used for each constituent (Standard

TABLE 1. TYPICAL NITROBACTER BIOASSAY DOSE-RESPONSE RESULTS

<u>N<sub>2</sub>H<sub>4</sub> Conc</u>	<u>N<sub>2</sub>H<sub>4</sub> Dose</u>	<u>Response</u>
mg/l	ug N <sub>2</sub> H <sub>4</sub> /mg TSS	% NO <sub>2</sub> <sup>-</sup> Removal vs Control
1.8	9.6	94
1.8	10.2	88
4.5	16.8	85
4.5	25.1	85
9.0	55.2	57
18.0	88.9	54
18.0	93.4	39
22.5	140.4	50
23.3	64.0	48
26.0	49.1	27
26.5	107.7	46
31.8	97.8	62
35.4	102.8	34
45.0	235.8	16
45	270.3	15
82	365	0
237	893	0

Methods for  $\text{NO}_2$  and Specific Ion meter for  $\text{NO}_3$ ) and the relatively small amounts of hydrazine degraded prohibited supporting any hypotheses as to the fate of hydrazine nitrogen in the Nitrobacter bioassay.

We encountered a problem with the analysis for hydrazine at the beginning of the bioassays. Stock hydrazine solutions were made up and standards run using the method of Watt and Chrisp (reference 15). Standards were also prepared at the concentrations to be used in the bioassay with nitrate solution rather than distilled water. Finally, hydrazine was analyzed from samples taken from the flasks containing living and killed bacteria about 5 minutes after the bacteria were introduced into the solution. The standards, the hydrazine in nitrite solution and the killed bacteria solution would all yield the same level of hydrazine within 5 percent. However, the solution of living bacteria would usually yield results about 10 to 15 percent lower than the others. This seems to indicate that there was a rapid initial reduction of hydrazine when the bacteria were first introduced and at a rate that was not sustained during the remainder of the bioassay. Consequently, a decision had to be made as to what was to be hydrazine concentration designated as the "before bioassay" concentration. We chose to use a concentration measured after the bacteria were introduced into the solution and after a 15 minute mixing and equilibrium period had elapsed. Therefore, it is possible that much more hydrazine was degraded in the bioassays than we report.

An attempt was made to account for the hydrazine degraded in the Nitrobacter using  $^{15}\text{N}$  labeled hydrazine with high vacuum techniques. The results were not conclusive as only about 7 to 10 percent of the hydrazine degraded was accounted for as  $^{15}\text{N}_2$  gas. Again, the problem was with the small amounts of hydrazine degraded in a non-lethal bioassay. However, the application of  $^{15}\text{N}$  labeled hydrazine in future work looks promising as a means to determine the fate of the hydrazine nitrogen if the Nitrobacter concentration used is high enough to produce a high degree of hydrazine degradation or if other bacteria populations can achieve satisfactory results.

#### D. NITROSOMONAS-NITROBACTER BIOASSAY STUDIES

A mixed culture of Nitrosomonas-Nitrobacter was selected for continued bioassay work for several reasons. First, this group offers all the advantages of the Nitrobacter as outlined earlier. Second, this mixed population utilizes substrate at a level lower in the nitrogen oxidation state than hydrazine and could conceivably metabolize hydrazine for energy. Third, the literature reports that Nitrosomonas is more resistant to various toxic agents than Nitrobacter including hydrazine (reference 14) and could possibly degrade sufficient hydrazine at sub-lethal levels to stand out significantly in any nitrogen balance attempt.

The culture growth and bioassay procedures were the same for this culture as for the Nitrobacter culture except for the following:

1. Feed consisted of 15 mg/l N as  $(\text{NH}_4)_2\text{SO}_4$ , 0.9 mg/l P as  $\text{NaHPO}_4 \cdot \text{H}_2\text{O}$  and 400 mg/l alkalinity as  $\text{NaHCO}_3$ . The alkalinity provided a neutralization capability for the hydrogen ions generated by the culture and insured a neutral pH.

2. Initial  $\text{NH}_4$  and  $\text{NO}_3$  determinations were made on replicate solutions which were analyzed immediately. Final  $\text{NH}_4$  and  $\text{NO}_3$  determinations were made on the contents of each bioassay flask after filtration.  $\text{NO}_2$  analysis was made on each bioassay solution.

3. Killed bacteria were included in every bioassay.

The Orion Specific Ion meter method was used for  $\text{NH}_4$  and  $\text{NO}_3$  determination because hydrazine presented strong interferences when routine wet chemistry methods were used as outlined in Standard Methods. This compromised the results somewhat because surrogate samples had to be used to determine the "before" levels of both nitrogen species rather than use the contents of the actual bioassay flasks themselves as the  $\text{NH}_4$  procedure calls for pH 10 or higher. In addition, the nitrogen balance was not as tight as desired because of this and the fact that the nitrite analysis did allow direct sampling of the bioassay solutions at the start and end of the bioassay.

The results of some preliminary bioassays are included in Table 2. If, as before, toxicity is defined as 50 percent inhibition of substrate removal rate for those solutions containing hydrazine, this would indicate a range of about 100 to 150 mg/l

TABLE 2. TYPICAL MIXED NITROSOMONAS-NITROBACTER DOSE-RESPONSE RESULTS

<u>N<sub>2</sub>H<sub>4</sub> Conc</u>	<u>N<sub>2</sub>H<sub>4</sub> Dose</u>	<u>Response</u>
mg/l	ug N <sub>2</sub> H <sub>4</sub> /mg TSS	% NO <sub>3</sub> <sup>-</sup> Removal vs Control
3.3	8.0	105
4.3	10.5	100
4.6	8.9	118
7.5	18.2	112
9.3	21.1	106
9.5	28.9	115
14.1	35.2	94
14.3	29.2	118
19.1	52.9	98
19.4	53.3	81
27.8	59.5	102
30.3	75.3	94
51.6	165.4	80
100.5	298.0	69
102.8	289.4	52
153.8	488.3	39
203.8	505.8	32
206.1	592.3	34

(300-500 ug  $N_2H_4$ /mg TSS). It is interesting to note that Tomlinson et. al. defined toxicity at 75 percent of normal substrate removal rate which occurred at 58 mg/l. Our results agree quite well with their findings.

Unlike the Nitrobacter bioassays, some substrate was lost in the presence of killed bacteria during the tests and was in the order of a 20 percent reduction over 3 to 6 hours (Nitrobacter tests ran 2 to 3 hours). This apparent loss is believed related to chemical and physical changes over time and to the degree of variation inherent in the specific ion analytical method itself.

Toxicity to the Nitrobacter was noted in these bioassays by an accumulation of nitrite and an absence of significant nitrate concentrations at the close of the bioassays compared to the controls. This occurred at concentrations below those toxic to the Nitrosomonas and is comparable to the data generated in the Nitrobacter tests. At high concentrations of hydrazine, we found as with the Nitrobacter tests, that hydrazine will interfere with nitrite analysis when the hydrazine to nitrite concentration ratio is about 20 to 1. Consequently, our nitrogen balance data indicates unrealistically low levels of final nitrite for those solutions containing above 75 mg/l hydrazine.

The nitrogen balance attempt for this mixed culture was more productive than that for the Nitrobacter studies because a greater amount of hydrazine could be degraded at levels not lethal to this mixed population. Table 3 shows the nitrogen balance for a bio-

TABLE 3. NITROGEN BALANCE FOR NITROSOMONAS-NITROBACTER BIOASSAY #9 CONDUCTED 5 FEB 1979

$\text{N}_2\text{H}_4$ Conc mg/l	TSS mg	% Response %	$\text{NH}_4^+$ Lost mg/Day	$\text{N}_2\text{H}_4$ Lost mg/Day	$\text{NO}_2^-$ Gain mg/Day	$\text{NO}_3^-$ Gain mg/Day	Net Balance mg/Day
Control A	32.3	100	3.80	-	2.58	1.42	-0.20
Control B	33.4	100	3.96	-	2.48	1.58	-0.10
9.5 mg/l	33.0	115	4.51	2.03	3.13	0.12	-0.77
153.8 mg/l	31.5	39	1.46	3.26	.36	-0-	-4.36
206.1 mg/l	34.8	34	1.40	4.37	.26	-0-	-5.31
10.2 mg/l (Killed bacteria)	44.1	15	.78	-0-	-0-	-0-	-0.78

NOTE: All gains/losses as mg nitrogen per day.

assay conducted recently. It is typical of all other bioassays. As can be readily noted for the controls and killed bacteria solution, a tight nitrogen balance has not been achieved. In addition, as was mentioned earlier, at high concentrations of hydrazine, there is an interference in the nitrite test which results in a lower than true nitrite concentration. Since high concentrations have proven toxic to Nitrobacter in earlier studies, one would expect that the true nitrite concentrations would not exceed the loss of ammonia. Overall, it would appear that there is some support for our hypothesis that the hydrazine degraded is not metabolized to ammonia, nitrite or nitrate. Most likely it is metabolized to nitrogen gas by the Nitrosomonas just as it has been found converted to nitrogen by other organisms, notably the rat (reference 10). The significant levels of hydrazine degraded in these bioassays indicate that our best choice for  $^{15}\text{N}$  labeled hydrazine studies is this mixed group of nitrifiers.

#### E. ANAEROBIC BACTERIA BIOASSAY STUDIES

The third group of common bacteria population utilized were the mixed group of acid formers and methane formers found throughout the environment and especially the digester tanks at wastewater treatment facilities. In fact, the batch test reactors were seeded with a mixture of 50 percent primary digester sludge and 50 percent warm tap water. Twelve one liter glass bottles were filled with 600 milliliters of the sludge-water mixture and two days allowed for the facultative bacteria to consume the oxygen

introduced during the seeding process. The culture procedures were similar to those outlined by Metcalf and Eddy (reference 8). Temperature was maintained at 35°C and daily gas production monitored as an indicator of toxicity. All twelve reactors had a mean cell residence time and hydraulic detention time of 20 days which was maintained by withdrawing five percent of the reactor volume daily and replacing this with an equal volume of substrate. Concentrated waste activate sludge was used as substrate of about 25,000 mg/l. A 15 day period was allowed for the reactors to establish steady state before hydrazine was introduced.

These batch tests served as initial screening for the levels of hydrazine which would prove toxic to this mixed group of bacteria. The pH of all reactors was monitored to provide an indication as to which group, acid formers or methane formers, or both would be affected by the hydrazine. Stock hydrazine was neutralized and introduced in volumes ranging from 1 to 20 milliliters just prior to the daily feed routine. No attempt was made to analyze the reactor contents for hydrazine due to the vast amount of organic and refractory material present as interferences. Table 4 show the hydrazine concentrations employed and the results. Toxicity is expressed in terms of percent gas production of the hydrazine units versus that for the 6 controls. Although Table 4 also lists the dosage of hydrazine on a weight per weight basis as we did for the nitrifiers, we are uncertain as to the actual percent of the 25,000 mg/l total suspended solids in the reactor (50 percent volatile) which were actually active bacteria.

TABLE 4. RESULTS OF ANAEROBIC BACTERIA BATCH TESTS

Reactor	N <sub>2</sub> H <sub>4</sub> Conc (mg/l)	N <sub>2</sub> H <sub>4</sub> Dose ( $\mu$ g N <sub>2</sub> H <sub>4</sub> /mg TSS)	Daily Gas Production as Percent of Controls						Lowest pH (Day)
			Day 1	Day 2	Day 3	Day 4	Day 5	Day 6	
1	2.7	0.13	76	102	105	101			6.9 (1)
2	13.3	0.67	76	52	70	67	74		6.3 (1)
3	133.3	6.1	48	30	19	10	19		6.6 (3)
4	400	18.7	44	6	4	3	6		6.6 (3)
5	668	34.0	46	11	5	5			6.4 (3)
6	1667	97.1	32	3	0	3			6.3 (3)
7	Control	None	108	100	96	97	97		7.0
8	Control	None	107	104	91	113	97		7.0
9	Control	None	100	112	103	105	105		7.0
10	Control	None	102	96	110	88	103		7.0
11	Control	None	97	93	104	98	102		7.0
12	Control	None	92	94	96	98	97		7.0

The data in Table 4 would indicate that recovery has taken place for the lowest two doses of hydrazine. For the lowest dose, the 6.9 pH occurring on day 1 would suggest that both the acid formers and methane formers were lightly upset but recovered about the same time. For the second lowest dose, a pH of 6.3 followed by recovery indicates that hydrazine seriously upset the methane formers and their ability to utilize the continued production of volatile acids. The other four reactors showed serious upset of both populations. The results of this initial screening test of anaerobic bacteria will serve as the basis for additional studies perhaps including  $^{15}\text{N}$  labeled hydrazine.

#### F. CONTINUING BIOASSAY STUDIES

Work has not yet begun on the denitrifier bioassays as the culture is still in its initial growth phase. This should begin after initial screening tests have been conducted. Depending upon the amount of hydrazine degraded,  $^{15}\text{N}$  labeled hydrazine studies may be warranted. The high vacuum approach lends itself very well to both aerobic and anaerobic studies. Sulphur hexafluoride replaces the 80 percent nitrogen found in the atmosphere and pure sulphur hexafluoride can be used under anaerobic conditions. The anaerobic system has the additional advantage in that since oxygen is completely eliminated, the problem of false mass numbers of 28 due to untrapped CO is reduced.

Although  $^{15}\text{N}$  studies may prove useful in identifying the hydrazine degradation products, the mechanism of the toxicity is

still not certain. Consequently, a brief literature review of possible toxicity mechanisms is presented as an appendix to this paper rather than in the body itself.

### III. CONCLUSIONS

To date, the following conclusions can be drawn concerning the toxicity of hydrazine to bacteria:

1. Hydrazine is toxic to Nitrobacter at 20 to 30 mg/l when toxicity is defined as 50 percent inhibition of the normal substrate removed rate.
2. Hydrazine is toxic to the mixed Nitrosomonas-Nitrobacter nitrifying bacteria at concentrations of 100-150 mg/l with toxicity defined as above.
3. Hydrazine is toxic to the mixed group of anaerobic bacteria (methane formers and acid formers combined) at about 133 mg/l toxicity defined as above.
4. A nitrogen balance for the Nitrosomonas-Nitrobacter bioassays gives support to the hypothesis that Nitrosomonas can metabolize hydrazine to nitrogen gas.

## APPENDIX A

### POSSIBLE TOXICITY MECHANISMS AS REPORTED IN THE LITERATURE

The literature was reviewed in an attempt to determine what possible sites for inhibition by hydrazine were possible and what mechanisms had been reported. Hydrazine has been used as an inhibitor for many years in the field of biochemistry. However, hydrazine was employed often as a tool so that other biological mechanisms not related to the hydrazine activity could be studied in detail. Consequently, little is reported as to how hydrazine inhibits or how hydrazine may be metabolized. This literature search has been initially limited to the nitrification process involving Nitrosomonas and Nitrobacter.

In high concentrations, hydrazine is used in protein analysis. When proteins are treated with anhydrous hydrazine, only C-terminal amino acids are cleaved from the protein and are released as acylhydrazines and amines (reference 1).

At least one site for hydrazine inhibition of Nitrosomonas is known and reported extensively in the literature (references 2, 3, 6, 9, 12, and 13). Intact cells will oxidize ammonia to nitrite with hydroxylamine ( $\text{NH}_2\text{OH}$ ) as an intermediate in the process. The conversion of hydroxylamine to nitrite is rapid and thought to provide the free energy for the first step. Hydrazine in the concentration range of 3.2 to 32 mg/l reportedly inhibits the process and hydroxylamine accumulates. Hydroxylamine itself is toxic at 28 mg/l (reference 17).

Considerable work has also been done with various portions of cell free constituents of Nitrosomonas and the results are somewhat clouded. Ritchie and Nicholas (reference 12) and Anderson (reference 2) have shown that in addition to the hydroxylamine ( $\text{NH}_2\text{OH}$ ), other intermediates or side reaction metabolites of the oxidation of ammonia to nitrite include the nitroxyl form ( $\text{NOH}$ ), hyponitrite ( $\text{N}_2\text{O}_2\text{H}_2$ ), nitric oxide ( $\text{NO}$ ) and nitrous oxide ( $\text{N}_2\text{O}$ ). Both oxidase and reductase activity has been demonstrated under aerobic and anaerobic conditions. This would imply that the nitrifying bacteria might also become denitrifying bacteria (reference 13). Other researchers (reference 11) have implicated the electron transport system of Nitrosomonas as susceptible to inhibition by hydrazine.

As far as the fate of hydrazine in the Nitrosomonas activity is concerned, Anderson (reference 2) has indicated that it probably competes with hydroxylamine and is dehydrogenated. On the other hand, Nicholas and Jones (reference 9) think that the inhibition of nitrite formation is due to competition with hydroxylamine for a common acceptor such as cytochrome C. Others have pointed to the electron transport system as possibly being vulnerable to hydrazine inhibition but have not agreed on the specific system or systems involved.

We have demonstrated that hydrazine is inhibitory and toxic to Nitrobacter and to Nitrosomonas and this follows what others have reported (references 5 and 7). However, the literature does not

suggest any mechanism for such a reaction. If the electron transport system in Nitrosomonas is suspect, it would appear reasonable to propose that the same system might be affected by hydrazine in Nitrobacter. However, at this point this is only speculation on our part.

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PAPER NO. 6

MONITORING HYDRAZINE VAPORS IN AIR  
USING A CHEMILUMINESCENT ANALYZER

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INTRODUCTION

The U.S. Air Force School of Aerospace Medicine (USAFSAM) is involved in exploratory development of methods and instrumentation for the measurement and detection in air of the three hydrazines, hydrazine itself (Hz), monomethylhydrazine (MMH), and unsymmetrical dimethylhydrazine (UDMH). This report is concerned with the hydrazine development program and is divided into two parts. Part 1 is an overview of USAFSAM efforts and Part 2 is a technical report on the in-house testing and evaluation of a breadboard model real time continuous hydrazine monitor which used chemiluminescence as its basis for detection.

PART 1. USAFSAM EFFORTS

All of the hydrazine monitoring development efforts are a result of the high toxicity of the hydrazine which impose low limits on permitted personal exposure concentrations. Table 1

lists the Air Force Occupational Safety and Health (AFOSH) exposure standards. AFOSH standards are based on the accepted American Conference of Governmental and Industrial Hygienist (ACGIH) values for a time-weighted average (TWA) 8-hour work day. National Institute for Occupational Safety and Health (NIOSH) proposed TWA's are listed for comparison and to indicate requirements which could be placed on exposure to hydrazine vapor in user and handler environments in the near future.

Using Table 1 exposure values as a design guide, USAFSAM is developing several hydrazine detection/monitoring concepts, both under contract and in-house (Table II). At the same time, there is an ongoing test and evaluation program for commercially available hydrazine detection instrumentation (Table III).

TABLE I. TWO STANDARDS FOR HYDRAZINE EXPOSURE (PPM)

	<u>AFOSH</u>	<u>NIOSH (Proposed)</u>
Hydrazine	0.1	0.03
MMH	0.2	0.04
UDMH	0.5	0.06

TABLE II. CURRENT USAFSAM DEVELOPMENT EFFORTS IN  
HYDRAZINE DETECTION/MONITORING

1. Chemiluminescence
2. Electrochemical
3. Gas Filter Correlation (IR)
4. Solid Sorbent Sampling/Wet Chemistry Analysis
5. Passive Personal Dosimeter

TABLE III. CURRENT USAFSAM T&E OF COMMERCIALY AVAILABLE  
HYDRAZINE DETECTION INSTRUMENTATION

1. Electrochemical Analyzer, Energetic Sciences, Incorporated  
85 Executive Blvd., Elmsford, NY 10523.
2. Area and personal dosimeter tape monitors, MDA Scientific, Inc.,  
808 Bussee Hwy., Park Ridge, IL 60068
3. Solid State Detector, International Sensor Technology,  
3201 South Halladay Street, Santa Anna, CA 92705
4. Photoionization Detector, HNU Systems Incorporated  
30 Ossipee Road, Newton, MA 02164

The on-going programs listed in Table II include area and personal monitoring techniques. Chemiluminescence produced by the reaction between the hydrazines and ozone is a detection concept discussed in detail in Part 2 of this paper. A second effort is a contract with Interscan Corp., Chatsworth, CA to build a real-time electrochemical analyzer that meets TWA standards for all three hydrazines. It differs from commercially available electrochemical analyzers mainly in its "solid matrix electrolyte" sensor which is not adversely affected by instrument position or a need for daily rehumidification. Barringer Ltd., Ontario, Canada is under contract to develop a gas filter correlation spectrophoto-

meter (GFCS) scheduled for May 1979 delivery. The GFCS used a nondispersive infrared (IR) technique and is an area monitor that has unique potential for long path (line of sight) monitoring. In-house development of an area/personal dosimeter technique involves use of a solid sorbent (sulfuric acid impregnated firebrick) sampling tube for collection of air-borne hydrazine, MMH, and UDMH vapors. Samples are analyzed using the para-dimethylaminobenzaldehyde (PDAB) method for hydrazine and MMH and the trisodium pentacyanoaminoferroate (TPF) method for UDMH. Sensitivity for the hydrazine in 15 liter air samples is on the order of 0.01 ppm for these wet chemical methods. The final development is a passive personal dosimeter designed to be worn on a person for an 8-hour working period. Analysis of the dosimeters after exposure is done by derivatization/gas chromatography or wet chemistry (PDAB) to give total time-weighted-average values. The dosimeters have been shown useful only for hydrazine measurements; MMH and UDMH testing are not yet complete. Test and evaluation of the dosimeters are scheduled for completion by January 1980.

Of the commercially available hydrazine detection instruments, the electrochemical analyzer and tape monitors have adequate sensitivity to detect the hydrazines to 0.1 ppm but are somewhat prone to interference by contaminants such as ammonia. Ammonia interference would be a problem around hydrazine monopropellant fueled rocket motors (e.g., F-16 emergency power unit) where ammonia is a major exhaust product. The solid state and photoionization devices, as delivered, are very sensitive but are interfered

with by many chemical contaminants. This limits their usefulness to a higher concentration (>5 ppm) leak detection.

## PART 2. A CHEMILUMINESCENT HYDRAZINES ANALYZER

### INTRODUCTION

Preliminary studies at the Crew Environments Branch, USAFSAM, indicated an instrument could be designed to monitor hydrazine fuel vapors in real-time using the chemiluminescence reaction between the hydrazines and ozone. A contract with AeroChem Research Laboratories, Princeton, New Jersey demonstrated feasibility of the approach (reference 1) and resulted in a follow-on contract for a breadboard model analyzer (reference 2). A description and evaluation of the breadboard model and its performance are presented here.

### BACKGROUND

The breadboard chemiluminescent hydrazines analyzer is shown schematically in Figure 1. It is very similar to an NO<sub>x</sub> chemiluminescent analyzer (reference 3) and was in fact designed to also measure both NO and NO<sub>2</sub>. Operation of the analyzer is relatively simple. Air being monitored was drawn into the instrument at about 19 ml/sec, 6 ml of which was treated as sample while the remaining 13 ml was scrubbed in an activated alumina trap to remove water, amines, and hydrazines before passage through a discharge ozonator to produce ozone. Ozone concentration in the 13 ml airstream was about 0.2 percent at the ozone inlet of the

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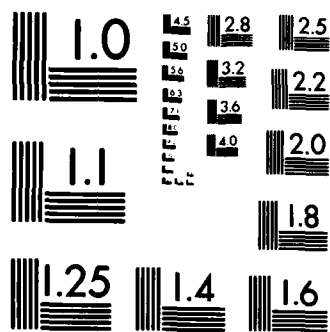
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reactor. Depending on the measuring mode, the 6 ml/sec sample was either passed directly into the sample inlet of the reactor for the measurement of hydrazines or through a phosphoric acid scrubber and NOx converter prior to entering the reactor for NOx measurement.

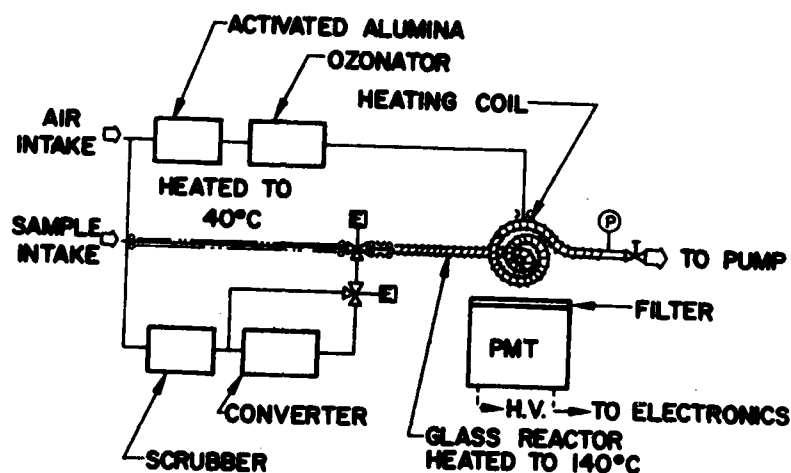


Figure 1. Schematic of Hydrazine/NOx Analyser

The reactor in which the reaction between ozone and the hydrazines occur was made of Pyrex®. To achieve good mixing and to have the initial reaction occur in the center of the photomultiplier tube (PMT), a 7 mm o.d. (6 mm inlets) flow tube curled into a spiral (5 cm diameter) was chosen for the reactor geometry. The volume achieved with this design was about 10 ml. Heating of the

reactor to 140-150°C to increase sensitivity and prevent reactor deposits was accomplished by applying voltage across 0.13 mm (5 mil) platinum wire wrapped along the length of the spiral.

Sample and ozone flow are controlled by critical orifices. Operating pressure of the instrument was approximately 220 Torr with small pressure changes having little effect on hydrazine response.

The detection system consisted of a 5 cm diameter trialkali photomultiplier tube (Centronics 4283) cooled to 10°C and an electrometer type amplifier. Zeroing and calibration potentiometers were provided for independent adjustment of the three hydrazines and the NO<sub>2</sub> measurements.

## EXPERIMENTAL

### Test Procedure

The experimental apparatus used for the testing described in this report is illustrated schematically in Figure 2. The three functional parts of the apparatus are: (a) a contaminant vapor generator, (b) a dilution subsystem, and (c) a delivery/analysis section. All test apparatus parts that contacted the hydrazines were made of pyrex glass.

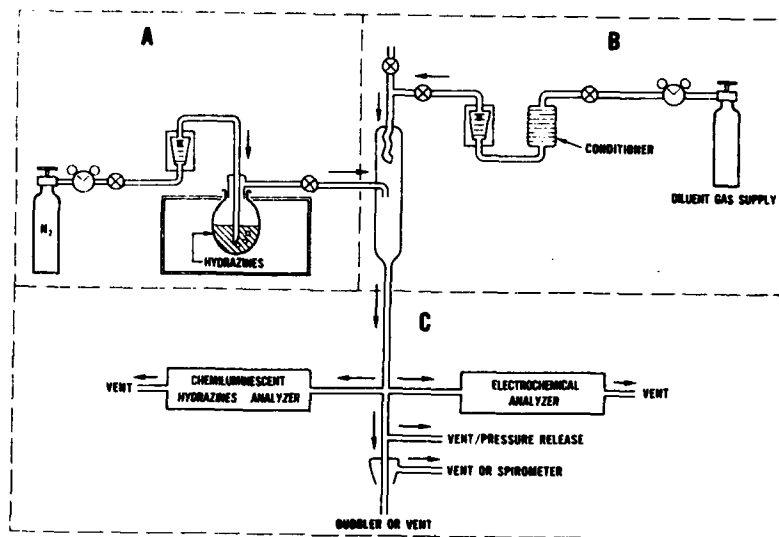


Figure 2. Schematic of the Test Apparatus:  
 (A) Contaminant vapor generator,  
 (B) dilution subsystem, and  
 (C) delivery/analysis section.

The hydrazines were produced in known concentrations in nitrogen in the generator subsystem (Figure 2A). Nitrogen, supplied by high pressure cylinders, was metered through a neat solution of the desired hydrazine contained in 100 ml round-bottom flask. The flask and its contents were kept at constant temperature by immersion in a thermostated circulating ethylene glycol bath. Hydrazine concentrations were calculated using vapor pressure-temperature data (reference 4) and flow rates obtained with an in-line calibrated rotameter. The nitrogen-hydrazine mix was delivered directly to the dilution system.

The dilution system (Figure 2B) was composed of a supply gas, flow control valves, calibrated rotameters, and a mixing chamber.

Supply gases used for dilution were high-pressure cylinders of laboratory-analyzed air. The glass mixing chamber was 3 x 16 cm.

Air samples containing the hydrazines were delivered to a manifold at flow rates between 3.5 and 35 liters per minute. The flow was split to provide sample to the chemiluminescent analyzer, an electrochemical analyzer, an intermittently used bubbler, and, at a minimum, an excess to vent to assure delivery of an adequate supply of sample gas at near-ambient pressures at all points.

#### Analysis

To assure generation and delivery of accurately known amounts of the hydrazines to the chemiluminescent analyzer, it was necessary to use a reference analytical method. Reference methods chosen and used were an electrochemical analyzer used for real-time measurement of hydrazine vapor concentrations between 1 and 100 ppm (reference 5) and a solid sorbent collection/wet chemistry technique (references 6, 7, and 8) between 0.01 and 5 ppm hydrazines.

The colorimetric method used for NO<sub>2</sub> was modified Jacob-Hocheiser procedure (reference 9).

## RESULTS AND DISCUSSION

A partial list of analyzer design and achieved specifications evaluated in this report is reproduced in Table IV. Each specification is presented and discussed in the order it appears on the list.

TABLE IV. HYDRAZINE ANALYZER SPECIFICATIONS

<u>Measurement</u>	<u>Design Goals</u>	<u>Achieved</u>
Contaminant	Hydrazine, MMH, UDMH, NO <sub>2</sub>	Same
Range	Hydrazines: 0-1, 0-10, 0-100 ppm	Same
Accuracy	> 10%	Same
Sensitivity	Hydrazines: 0.2 ppm	Hydrazine 0.015 ppm
	NO <sub>2</sub> : 5 ppm	MMH 0.04 ppm
		UDMH 0.07 ppm
		NO <sub>2</sub> 0.35 ppm
Response	10 seconds (show) 60 seconds (90%)	Same

Tests performed during this evaluation indicated that the light emitted from the reactions of all three hydrazines was linear with concentration between the lowest detectable values and about 100 ppm. These results are illustrated in Figure 3. Sensitivity of the analyzer to the three hydrazines differed with hydrazine being about 2.7 times that of MMH which was about 1.4 times as sensitive as UDMH.

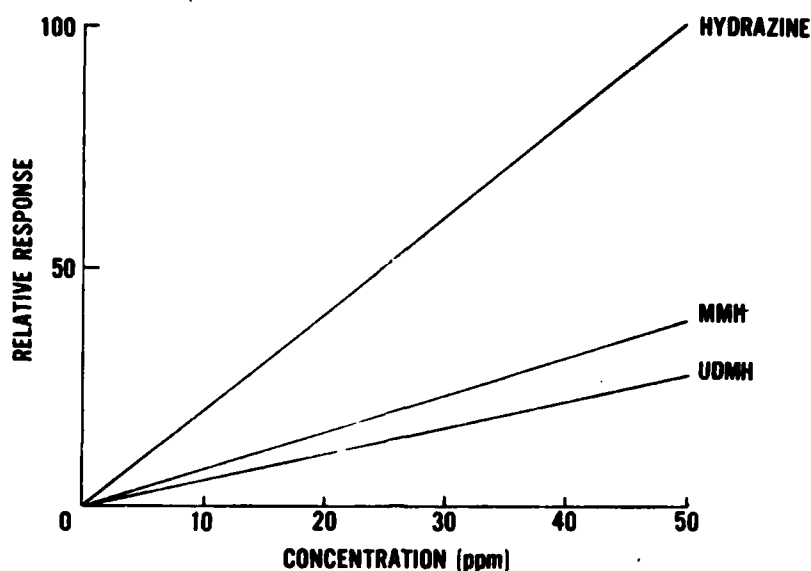


Figure 3. Relative Analyzer Response as Function of Hydrazine Concentration.

Accuracy of measurements for all three hydrazines at concentrations below 1 ppm was >10% with somewhat better results obtained at higher concentrations.

Typical recorder traces for low concentrations of hydrazine and UDMH in are reproduced in Figure 4. The two traces illustrated provide various pieces of information starting with a demonstration of the favorable signal to noise ratios observed even at the lowest detectable concentration for UDMH. Minimum detectable concentrations estimated from such traces are listed in Table IV and range from about 0.015 ppm for hydrazine (most sensitive) to 0.07 ppm for UDMH (least sensitive). Response and recovery (washout) times (100% in less than 1 minute) for both traces demonstrated adequate real-time monitoring potential. Heavy overloads (> 20 ppm) of hydrazine required longer recovery times before low levels (> 1 ppm)

hydrazine required longer recovery times before low levels ( $> 1$  ppm) of the hydrazines could be measured. This was partly due to wall adsorption effects that could be partly alleviated through the use of shorter heated sample lines.

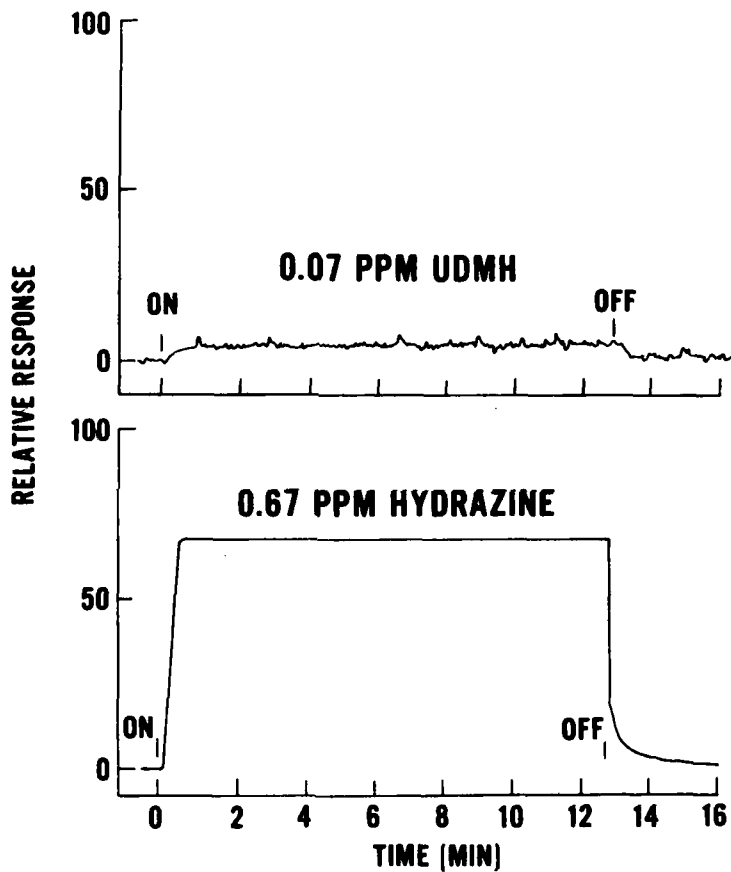


Figure 4. Chemoluminescent Analyzer Traces

Interference test results are presented in Table V with analyzer responses calibrated relative to hydrazine.

TABLE V. HYDRAZINE ANALYZER INTERFERENCE

<u>Interferant</u>	<u>Extent of Interference (% of Response in Hydrazine Mode)</u>
Water	-2 to -8/H <sub>2</sub> O
Ammonia	0
Methylamine	1.5
Propylamine	1.5
Aniline	7.0
SO <sub>2</sub>	0
NO	4
NO <sub>2</sub>	0
CO	0
CO <sub>2</sub>	0
Ethylene	10

Water interference was about -2 percent per 1 percent water for UDMH, -4 percent per 1 percent water for MMH, and -8 percent per 1 percent for hydrazine.

Potential interferants were tested individually using in-house prepared and analyzed samples. Concentrations of the contaminants delivered to the analyzer were generally between 10 and 25 ppm. Carbon dioxide was delivered at concentrations up to 1000 ppm.

Interference by the contaminants studied was minimal. Water was a problem in measurement of hydrazine but can be alleviated through calibration, temperature/humidity correction tables, and possibly by changes in the (ozonator air) to (sample air) flow

ratios. Ammonia, a common interferant in many hydrazine measurement techniques, did not interfere in this chemiluminescent method. None of the common air constituents and pollutants, except for NO, caused analyzer response. A background of NO can be measured and subtracted by use of the acid scrubber circuit, if desired. Actual NO interference (4 percent of hydrazine response) is not significant for most hydrazine monitoring operations because of the low background concentrations of NO.

Aliphatic amines produced negligible interference (less than 2 percent) with somewhat higher response recorded for the aromatic amines. The aromatic amines (for example aniline) and the olefins (such as ethylene) are potential interferants but are found in such low concentrations at any but special industrial or use sites that they will probably be of little concern to hydrazine monitors. Ethylene would be useful for dynamically calibrating the analyzer since its response relative to the hydrazines appears constant.

Nitrogen dioxide measurements were shown to be comparable with those made by a commercial NO<sub>x</sub> chemiluminescent instrument. The shorter wavelength band used for detection in the breadboard model caused a decrease in sensitivity from the usual and expected lower ppb range to about .350 ppm. This sensitivity difference was not enough to affect adequate performance (design goal was 5 ppm). Linearity and other factors, such as time of response, was also adequate and compared favorably with measurements made on our in-house commercial NO<sub>x</sub> analyzer.

## CONCLUSIONS AND RECOMMENDATIONS

The breadboard model hydrazine/NO<sub>x</sub> analyzer is useful for measuring all the hydrazines and NO<sub>2</sub> at presently required TWA exposure values with minimal interference and without modification. However, a more rugged instrument would be preferred for routine and field use. This requires a better utilization of space, more rugged and stable mounting of electronic components, and vibration-free mounting of the vacuum pump (we had to operate the pump external to the instrument at times).

For optimum development as a hydrazines analyzer, further simplification/modification is needed:

(1) Since it is not necessary to monitor for NO<sub>2</sub> in most applications, the NO<sub>2</sub> converter/circuit can be eliminated.

(2) Space utilization should include arrangement of component parts to permit the shortest sample inlet lines possible.

(3) Changes in reactor geometry should be made to time discriminate between NO interference and the hydrazine signals. This would permit use of an optical filter with a band-pass extended to higher wavelengths and should result in better hydrazine sensitivity.

(4) Before building a prototype analyzer, a study should be made of the effects on hydrazine sensitivity and interference problems of eliminating the blue filter.

(5) Commercially available ozonators should be evaluated for workmanship, size, ozone output, operating voltage, and attendant stability before adopting an ozonator for inclusion in a prototype instrument. The ozonator in this study was not as stable and reliable as others used in this laboratory; therefore, it should be determined whether it was the specific unit we used or a problem common to the brand/type.

Adequate performance of the breadboard model will be followed by a hardware study contract during 1979 to produce three prototype hydrazine analyzers. The three prototypes should be ready for field testing in January 1980.

## SUMMARY

This report presents (1) an overview of ongoing work at the USAF School of Aerospace Medicine in the area of hydrazine vapor monitoring and (2) results from the test and evaluation of a breadboard model chemiluminescent hydrazine analyzer. Ongoing work discussed covers in-house and contractual development efforts in hydrazine measurement methods (area and personal exposure monitoring) including continuous real-time instrumental techniques. The breadboard model chemiluminescence hydrazine analyzer tested and evaluated was an instrument developed and built for the Air Force by AeroChem Research Laboratories, Princeton, New Jersey. This real-time analyzer responded to hydrazine, monomethylhydrazine (MMH) and unsymmetrical dimethylhydrazine (UDMH). Its principle of operation is the measurement of the intensity of light produced by a reaction of a sample airstream containing one of the hydrazines with a second airstream containing in situ generated ozone. In-house evaluation showed the analyzer, as received, to have a linear range of 0-100 ppm for all three hydrazines. Sensitivity achieved was 0.02 ppm hydrazine, 0.05 ppm MMH, and 0.07 ppm UDMH. Interference by the aliphatic amines and nitric oxide was less than 4 percent of hydrazine response. Detailed evaluation of the analyzer's performance, as well as a discussion of parameter and component changes necessary in redesigning the instrument for portability and increased ruggedness are presented.

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PAPER NO. 7

IDENTIFICATION OF THE PARTIAL  
OXIDATION PRODUCTS OF HYDRAZINE,  
MONOMETHYLHYDRAZINE AND UNSYMMETRICAL  
DIMETHYLHYDRAZINE FROM OZONATION

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INTRODUCTION

Monomethylhydrazine (MMH) and unsymmetrical dimethylhydrazine (UDMH) rocket fuels, along with hydrazine (Hz) pose an environmental hazard from accidental spills or as contaminants of wash water from clean up of tank cars. Ozone oxidation is one of the possible treatment processes for hydrazine-contaminated waters.

The objective of this study (see Acknowledgements) were to establish the stoichiometry and kinetics of the ozone oxidation of Hz, MMH, and UDMH, to identify the partial oxidation products from the ozone oxidation, and to ascertain the aquatic toxicity of the treated water with fathead minnows and Daphnia magna.

The objectives were accomplished by a team of personnel including a chemical-environmental engineer, chemists, and aquatic biologists. The engineer was responsible for overall process design and optimization, with the required data being furnished by the chemists and aquatic biologists. Analyses of hydrazine fuels and partial oxidation products, together with gross parameter measurements such as COD, TOC, and nitrates, were essential in establishing the kinetics of the process as well as in establishing optimum reactor operating conditions. Aquatic biologists used static acute toxicity experiments to evaluate the toxicity of Hz, MMH, and UDMH before and after ozonation.

This paper will describe some of the screening tests made to assess the quantity and nature of the partial oxidation products. The structure and type of team approach utilized in this project are appropriate for treatability studies that are to be conducted on any wastewater intended for direct or indirect water re-use.

#### HYDRAZINE CHEMICAL TREATMENT

The basic apparatus used for all experiments is presented in a process flow diagram shown in Figure 1 and employed a Grace ozonator Model LG-2-L2 to produce ozone from air or oxygen.

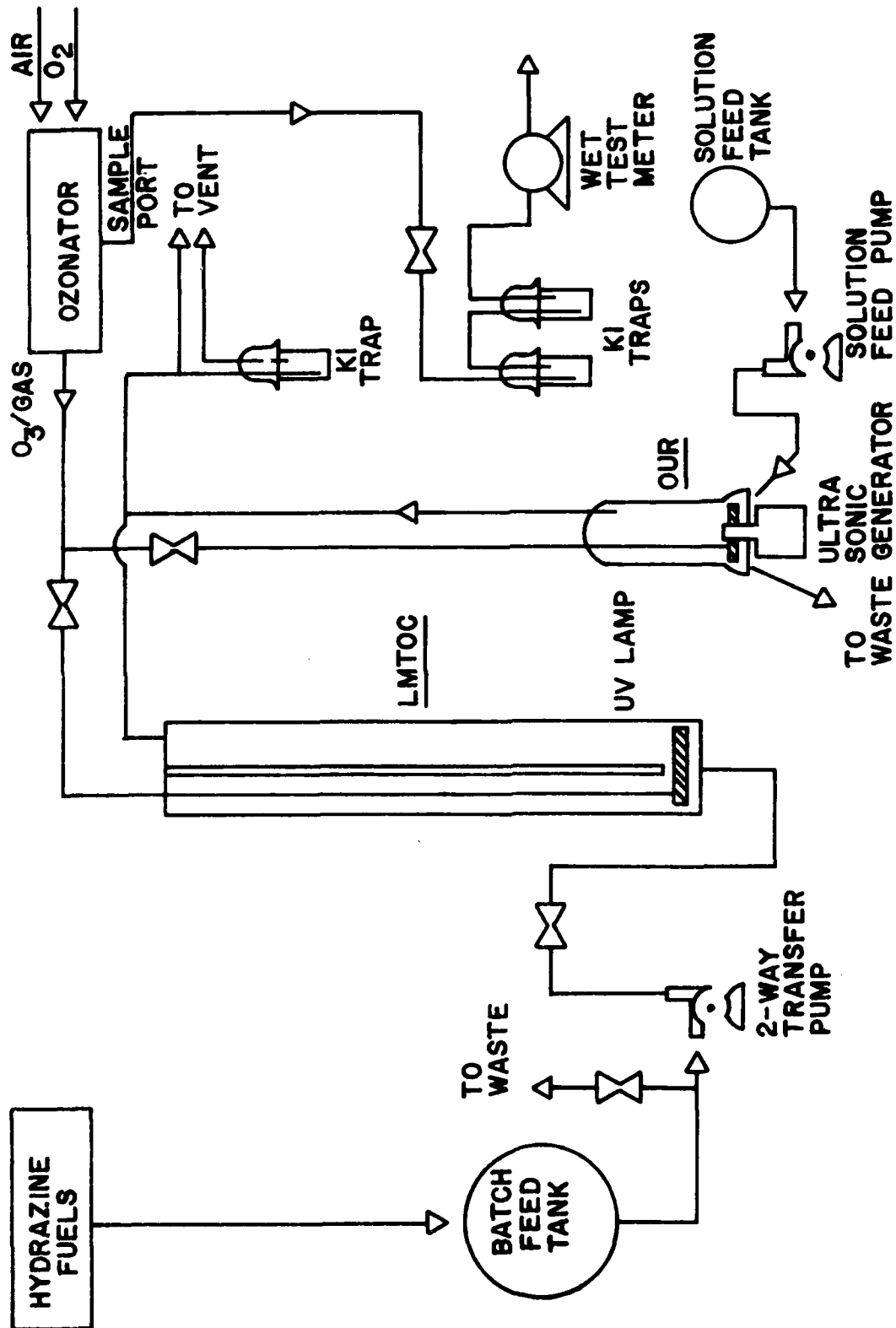


Figure 1. Process Flow Diagram

For runs when an ozone concentration of 13 mg/l air or less (approximately 1 percent ozone in air) was desired, air was the ozonator feed gas. Air was compressed in a Puregas Compressor Model 4 HCJ-12-M 400 x and passed through 1/4" I.D. stainless steel tubing to the ozonator at 15 psig. Tank oxygen, (extra-dry grade) was supplied to the ozonator in the same manner as the air. Oxygen feed gas permitted the production of higher concentrations of ozone (i.e., approximately 2 percent ozone in oxygen) than with air for the same electrical power input to the generator.

All experiments were conducted in a semi-batch mode, that is, a constant liquid volume and a continuous supply of gas. Two reactors were employed in this work. The primary reactor was the Life System Modified Torricelli Ozone Contactor (LMTOC). Also an ozone-ultrasonic reactor (OUR), constructed from pyrex glass and fitted for an ultrasonic generator, was utilized.

Solutions of Hz, MMH, and UDMH were prepared from fuel material and distilled water in 36 liter batches. Alkaline pH batches were buffered with sodium borate (0.01 M) while acidic batches were produced by adding concentrated hydrochloric acid (HCl) to the desired pH.

For all runs 30 liters of material were pumped to the LMTOC from the feed tank. During this transfer period of approximately 6 minutes, the reaction mass was air sparged to ensure homogeneity. Prior to initiation of ozonation, a sample was extracted at the mid-depth point in the column. Throughout each run, at appropriate

time intervals, samples were obtained at this sample tap for all analyses performed on liquids.

Five liters of solution were pumped to the OUR for each run through a one way valve. Liquid samples were obtained periodically from the reactor bottom through a stainless steel valve.

Ozone gas samples from the ozonator, the LMTOC and the OUR were passed through two potassium iodide (KI) traps in series. The first trap contained 300 ml of 2 percent KI while the second contained 100 ml of solution. Ozone gas samples were trapped exclusively in the first gas sampler, thus the second trap merely gave assurance that all of the ozone had been collected. Sample gas volumetric flow rates were measured with a wet test meter.

Hydrazine and monomethylhydrazine in the reactor were determined with an automated procedure based upon the colorimetric method of Watt and Chrisp (reference 1). A Technicon II Autoanalyzer® module was constructed for these analyses. Standard curves were constructed in the range of 0-1.5 mg/l of Hz, and 0-12 mg/l of MMH. Samples were diluted when necessary with glass distilled water using a Repipet® diluter. Replicate dilutions to 1/10 or 1/50 showed relative standard deviations of about 5-10 percent while recoveries of Hz and MMH spikes were 103-107 percent.

UDMH was determined by the colorimetric procedure of Pinkerton et. al. (reference 2), for the range of 0-60 mg/l. A Spectronic 700® spectrophotometer was used for this method and for the

dissolved ozone in water determination. Recovery of a UDMH spike added to an ozonated sample water was 93 percent with a range of 92-93 percent.

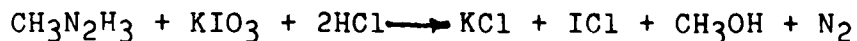
## RESULTS AND DISCUSSION

Ozonation of hydrazine effectively oxidized the compound and its reaction products, as shown by the Hz and COD data in Figure 2. While Bowen and Birley (reference 3) indicated that the main reaction between Hz and oxygen is:



ozonation produced a small yield of nitrate-N (2 percent of initial hydrazine-nitrogen). Nitrate was probably the product of ammonia oxidation, where ammonia was a side product of the main reaction shown above. Ammonia has, in fact, been found from the reaction between oxygen and hydrazine vapor (reference 4).

The ozonation of MMH also produced small quantities of nitrate-N (4 percent of initial MMH-nitrogen), as seen in Table 1. Possibly a side reaction was responsible for ammonia production as in Hz ozonations. The main reaction for oxidation for MMH would be expected to follow the stoichiometry of the familiar reaction with potassium iodate, used to determine MMH (reference 5).



This equation predicts that methanol, and hence TOC and COD, could remain after initial oxidation of MMH were complete. This was

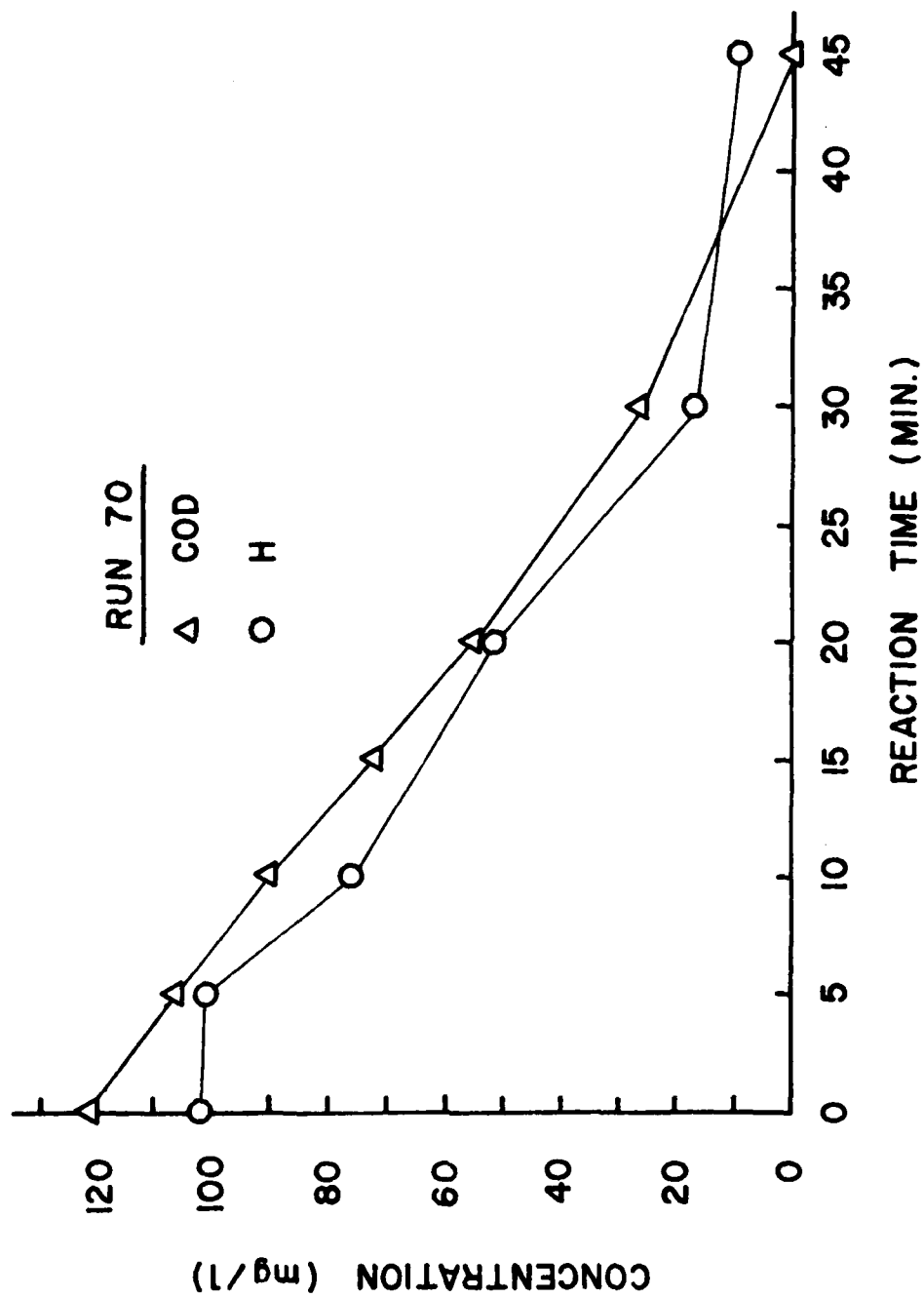


Figure 2. Change in Hydrazine and COD with Ozonation Time

actually the case in the ozonation run shown in Table 1. TOC and methanol both reached a maximum in 15 minutes, then decreased slowly thereafter. The initial unexpected increase in TOC was apparently related to the inability of the carbon analyzer to accurately measure the TOC of high-level MMH solutions. By the end of the run, the MMH was essentially gone, but 28 percent of the initial COD remained. Since methanol has been shown (reference 6) to react with UV-catalyzed ozone to form formaldehyde and formic acid before loss of TOC as carbon dioxide, the list of partial oxidation products expected from MMH ozonation should include: methanol, formaldehyde, formic acid, and formaldehyde monomethylhydrazone ( $\text{CH}_3\text{NHN}=\text{CH}_2$ ), formed by reaction between MMH and formaldehyde.

TABLE 1. CHARACTERIZATION RUN #43 (MONOMETHYLHYDRAZINE)

<u>TIME</u> <u>(Min)</u>	<u>MMH</u> <u>(mg/l)</u>	<u>METHANOL</u> <u>(mg/l)</u>	<u>TOC</u> <u>(mg/l)</u>	<u>COD</u> <u>(mg/l)</u>	<u>NITRATE-N</u> <u>(mg/l)</u>
0	114	<5	32	264	0.19
5	109	11	34	238	1.38
10	61	22	36	210	1.48
15	103	27	42	196	1.64
20	58	25	37	167	1.94
30	2.7	22	36	135	2.18
45	0.5	17	31	106	2.52
60	<0.2	11	25	73	2.86

As expected from MMH and Hz ozonations, UDMH also reacted with ozone to produce nitrate-N, at roughly 13 percent of the initial

UDMH-N concentration (Table 2). Although UDMH was reduced to about its detection limit after 35 min, 68 percent of the initial TOC and 40 percent of the initial COD still remained in solution. Some of this residual organic material was determined to be methanol. Figure 3 shows a gas chromatographic-mass spectrometric (GC/MS) analysis of the 35-min ozonated UDMH solution described in Table 2. Total ionization current and  $m/z = 42$  mass chromatograms are shown in Figure 3 for this sample and the two peaks were identified as N-nitrosodimethylamine (NDMA) and dimethylformamide (DMF).

TABLE 2. CHARACTERIZATION RUN #49-205  
(UNSYMMETRICAL DIMETHYLHYDRAZINE)

<u>TIME</u> <u>(Min)</u>	<u>UDMH</u> <u>(mg/l)</u>	<u>TOC</u> <u>(mg/l)</u>	<u>COD</u> <u>(mg/l)</u>	<u>NITRATE-N</u> <u>(mg/l)</u>
0	122	54	237	0.03
5	98	41	209	1.10
10	74	40	181	2.11
15	45	38	150	3.34
20	25	38	131	4.40
35	0.7	37	96	7.22

In order to produce higher concentrations of UDMH ozone reaction products, a 5600 mg/l solution of UDMH (run no. 60) was ozonated in a pyrex glass ultrasonic-ozone reactor.

Analysis of this 70-min solution by GC/MS showed 15 peaks on the total ionization current chromatogram in Figure 4. Of these 15

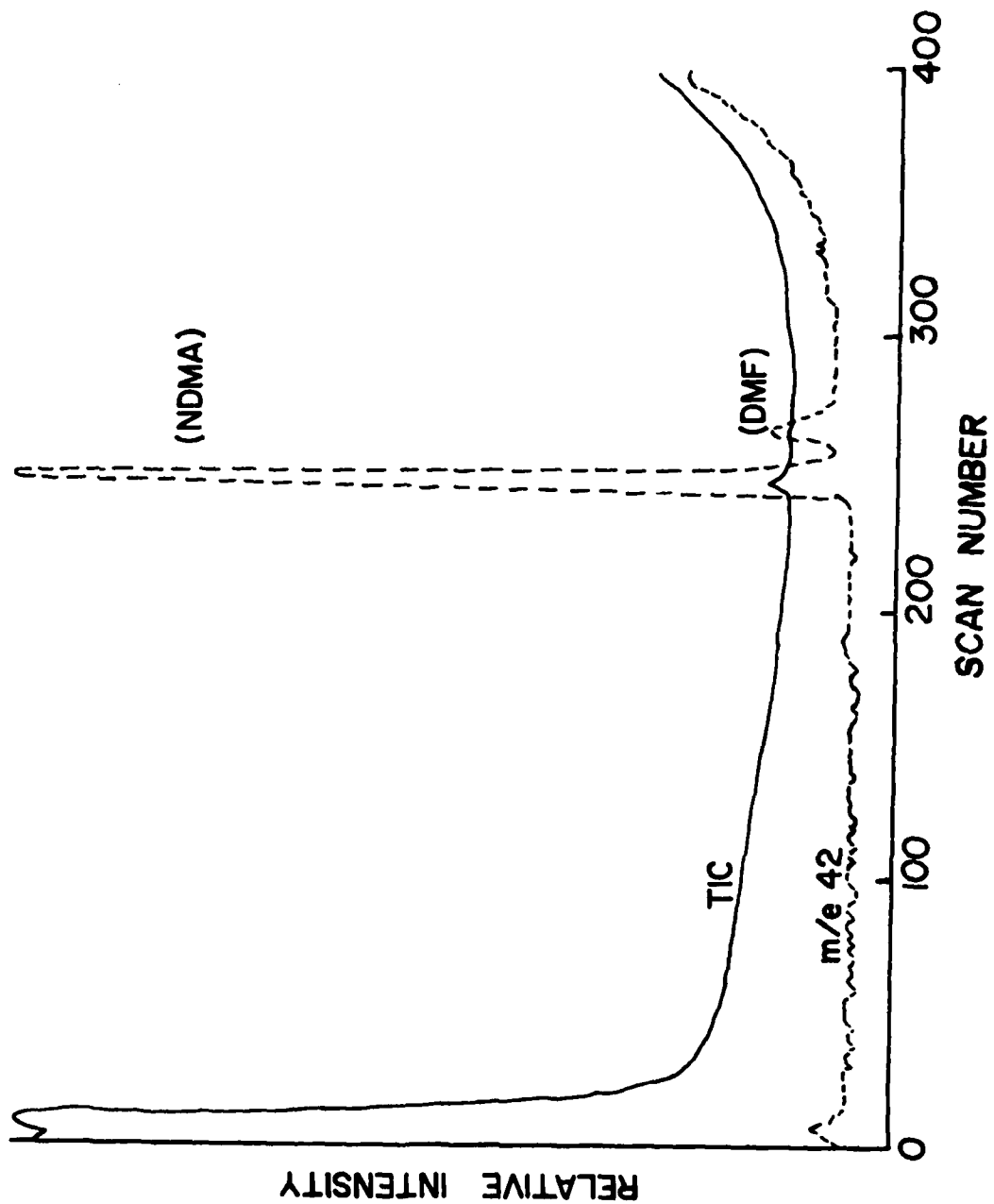


Figure 3. Total Ionization Current and m/e 42 Chromatograms for R49-205-35 min.  
Ozonated UDMH

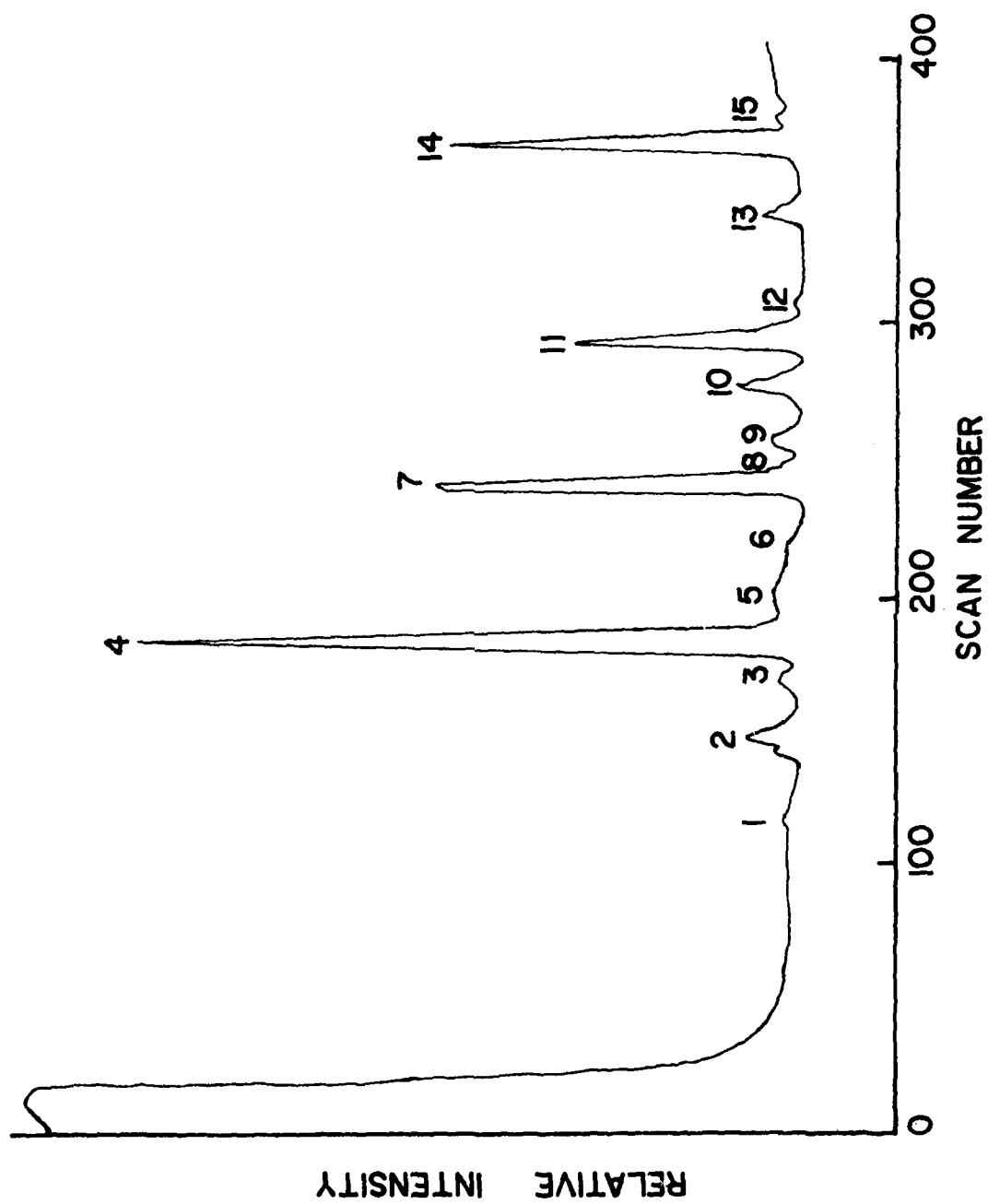


Figure 4. Total Ionization Current Chromatogram of R-60-70 min. Ozonated UDMH

peaks, seven were confirmed as those listed in Table 3. Methanol (see Figure 2) was not included in this list because it would have eluted before mass scanning had begun at 2 min after injection. Since methanol was present, formaldehyde and formic acid should also be expected from UDMH ozonation. Formaldehyde could react with UDMH to produce formaldehyde dimethylhydrazone, which was shown (peak #4 in Figure 4) to be a major product. Peak #7 (NDMA) was also significant product and is a known carcinogenic compound. Formaldehyde monomethylhydrazone, formaldehyde hydrazone, methylamine, dimethylamine, and NDMA have been identified by Loper (reference 7) as minor oxidation products of UDMH in the gas phase; however, neither the two amines nor formaldehyde hydrazone were identified as any of the peaks in Figure 4.

TABLE 3. COMPOUNDS IN OZONATED UDMH SOLUTION CONFIRMED BY GC/MS

<u>PEAK</u>	<u>COMPOUND</u>
1	Acetone (Instrument Background)
2	UDMH
3	Formaldehyde Monomethylhydrazone $\text{CH}_3\text{NHN}=\text{CH}_2$
4	Formaldehyde Dimethylhydrazone $(\text{CH}_3)_2\text{N}-\text{N}=\text{CH}_2$
7	N-Nitrosodimethylamine $(\text{CH}_3)_2\text{N}-\text{N}=\text{O}$
9	Dimethylformamide $(\text{CH}_3)_2\text{NCOH}$
10	Tetramethyltetrazene $(\text{CH}_3)_2\text{N}-\text{N}=\text{N}-\text{N}(\text{CH}_3)_2$

Aquatic toxicity assays with minnows and daphnids demonstrated the toxicity of the pure hydrazine fuels, as presented in Table 4.

The fuels showed LC<sub>50</sub> values of 4.5, 1.22, and 0.35 mg/l to minnows for Hz, MMH, and UDMH, respectively. Harrah (reference 8) has reported a value of 3.4 mg/l to sticklebacks (Gasterosteus aculeatus) for Hz solutions, in fair agreement with the 4.5 mg/l value found for fathead minnows. The toxicity of the fuels to Daphnia magna ranged from greater than 0.1 to less than 10 mg/l. Because the hydrazines were found to react with oxygen during bioassays, the actual LC<sub>50</sub> or EC<sub>50</sub> values due to pure hydrazine fuels may be even less than the values in Table 4.

If the 122 mg/l Hz solution used for ozonation run no. 43 were diluted to obtain the LC<sub>50</sub> (toward minnows) concentration of 4.5 mg/l, it would have to be diluted to  $(4.5/122) \times 100$  percent = 3.7 percent (v/v) with water. After ozonation of this Hz solution, however, the range-find LC<sub>50</sub> of the reaction products was reached at between 100 percent (v/v) (i.e., no dilution) and 50 percent (v/v) dilution with well water. Thus, the toxicity of the mixture of Hz partial oxidation products was less than the initial Hz solution. However, the borate buffer control (with 0.01 M  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ , or 3.81 g/l) also showed toxicity towards minnows of 7-7.5 g/l at 17°C in hard water. Because of such possible added toxicity from the sodium borate, it was not possible to determine if the partial oxidation products from Hz had any residual toxicity in these range-find tests.

Similar calculations indicated that the toxicity of MMH and UDMH solutions were reduced by ozonation. The data for these com-

pounds were not conclusive enough to determine whether there are any residual toxicity not explained by the borate buffer system.

The Daphnia full-scale bioassays of ozonated hydrazines also indicated that the toxicity of the pure fuels was reduced. Again, there was residual toxicity in the borate control, which obscured any residual toxicity which might have been due to the partial oxidation products. Anderson (reference 9) has reported that the threshold concentration of sodium borate for immobilization of Daphnia magna was much less than 240 mg/l.

TABLE 4. AQUATIC TOXICITY RESULTS

Compound	Fathead Minnow		Daphnia	
	pH	LC50	pH	EC50
H <sub>2</sub>	--	4.5 <sup>a</sup> mg/l	8.6	0.1 ≤ x <1 mg/l
H <sub>2</sub> +O <sub>3</sub>	7.5	50% ≤ x <100% v/v	7.0	12.5% ≤ x <25% v/v <sup>a</sup>
MMH	--	1.22 <sup>a</sup> mg/l	7.0	≤ 5.0 mg/l
MMH+O <sub>3</sub>	9.1	25% ≤ x <50% v/v	8.8	25% ≤ x <50% v/v <sup>a</sup>
UDMH	--	0.35 <sup>a</sup> mg/l	8.1	5.0 ≤ x 10.0 mg/l <sup>a</sup>
UDMH+O <sub>3</sub>	9.1	12.5% ≤ x <25% v/v	7.0	50% v/v <sup>a</sup>
	7.5	40% ≤ x <50% v/v		
O <sub>3</sub> + Borate	7.5	50% ≤ x <100% v/v	7.0	25% ≤ x <50% v/v <sup>a</sup>
O <sub>3</sub> + Borate	9.4	<50% v/v	--	--

a. Results of full scale 96-hr bioassays; all others are range-find bioassays.

## CONCLUSIONS

The purpose of these characterization studies was to give a preliminary screening of the residual mixture of compounds which may result when hydrazine fuel mixtures are ozonated to the point of complete removal of the hydrazine species.

The results of Hz, MMH, and UDMH ozonations showed relatively minor yields of nitrate, which was probably the oxidation product of ammonia. The ammonia may have been produced in a side reaction. Another possible route for nitrate may have been from nitrosamine oxidation; the UDMH ozonations, where NDMA was detected, did show a higher nitrate yield than seen from Hz ozonation, where N-nitrosamines could not have been produced.

Although methanol was the only organic oxidation product identified from MMH ozonation, GC peaks from at least four other compounds were seen when MMH was oxidized at a high concentration. Formaldehyde and formic acid are known ozonation products of methanol, so formaldehyde monomethylhydrazone may also be a product of MMH ozonation.

Methanol, formaldehyde dimethylhydrazone, formaldehyde monomethylhydrazone, N-nitrosodimethylamine, dimethylformamide, and tetramethyltetrazene were identified in UDMH ozonations. From methanol, formaldehyde and formic acid should also have been present although they were not identified in these studies.

Since the residual organic compounds from MMH and UDMH ozonation are expected to be amenable to ozonation, their concentrations

can probably be reduced by continued ozonation past the point of hydrazine fuel removal. Although aquatic bioassays indicated that ozonation to the point of fuel removal reduced the toxicity of the solutions, safe reuse of hydrazine fuel wastewaters will require such continued periods of ozonation.

#### ACKNOWLEDGEMENTS

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The authors wish to acknowledge the assistance of Mr William J. Cooper in the planning and coordination phases of the project. Also acknowledged are Dr Mark Warner, Steven Broich, and Sally Diehl for the aquatic toxicity work, Mr John Kaefer, Ms Jill Golden and Ms Iris Jones for their assistance with the chemical analyses, and Capt Joseph A. Zirrolli for GC/MS analyses.

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PAPER NO. 8

CHLORINOLYSIS TREATMENT OF HYDRAZINE IN  
DILUTE AQUEOUS SOLUTION

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ABSTRACT

The handling, transport, storage, and use of hydrazine (Hz), unsymmetrical dimethylhydrazine (UDMH), and monomethylhydrazine (MMH) can result in the generation of dilute aqueous solutions of these compounds along with traces of dimethylnitrosamine (DMNA).

The treatment chemistry and kinetics of these dilute aqueous solutions was investigated in the laboratory and with a 30 gal pilot reactor. On the basis of these results a process to treat a

minimum of 2,000 gal of contaminated wastewater per day was developed. The process is based on chlorinolysis catalyzed by ultra violet light. The process equipment and operating procedures are described.

## INTRODUCTION

The manufacture, handling, transport, storage and use of hydrazine fuels have the potential for the generation of wastewater containing hydrazines at concentrations which range in from a few ppm to several thousand ppm. In addition to the hydrazines there is a distinct possibility that there will be low concentrations of dimethylnitrosamine, either associated with the production of UDMH, or from air oxidation of UDMH.

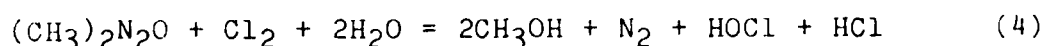
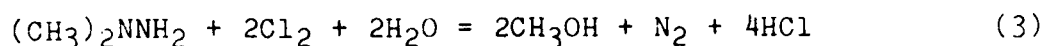
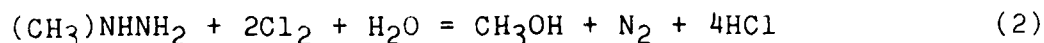
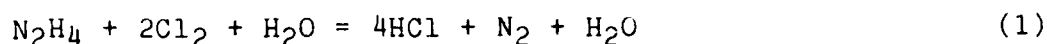
There has been a need for a safe, reliable and economic process for the treatment of these wastewaters. Several processes were considered and it was found that the ultra violet light catalyzed chlorinolysis had good potential for treatment of the wastewater.

## Candidate Processes

A variety of physical and chemical treatments methods for the removal of UDMH, MMH, Hz, and DMNA from wastewater have been studied in the laboratory. These processes include oxidation by ozone, air, sodium hypochlorite, chlorine, hydrogen peroxide, or by biological degradation. All processes had some disadvantage. The uv-chlorine process appeared to have the best potential and a treatment system was designed on the basis of this process.

### Chlorinolysis Process

Chlorine reacts with the contaminants according to the following reactions:



Thus four moles of Cl (2 moles of  $\text{Cl}_2$ ) are required for each mole of the hydrazine and two moles of Cl for each mole of DMNA.

Laboratory and pilot plant (30 gal) studies of reaction rates indicated the reaction between chlorine and the hydrazines was very fast but complete reaction of  $\text{Cl}_2$  and DMNA required either a large excess of  $\text{Cl}_2$  or a pH of 2 to 3. A large residual excess of chlorine presents problems in disposal of treated wastewater and in excessive chlorine usage. Operation at low pH enhances the possibility of nitrogen trichloride formation and presented control instrument problems since commercially available instruments required pH of about 5 for long term stable operation. Because of these problems, it was decided to utilize ultra violet light to increase the chlorinolysis reaction rate. Studies of the effect of light intensities on reaction rates indicated a light intensity of 1 watt/liter was 20 times as fast as a light intensity of 0.1 watt/liter. At a light intensity level of approximately 1 watt/liter and a chlorine concentration of 500 ppm the

concentration of DMNA decreased by one order of magnitude in 60 minutes.

#### Process Description

The process flow sheet is shown in Figure 1. The process utilizes a 10,000 gallon hold tank, a chlorinolysis reactor, a chlorine addition system, a nitrogen stripping system, a pH control system, and a  $\text{Na}_2\text{S}_2\text{O}_3$  neutralization system. The effluent is discharged to a holding pond and may then go to a biological treatment facility, to land spreading, or to a waterway.

The 10,000 gallon hold tank is used to collect the wastewater and to level out variations in the concentration for more consistent day-to-day operation of the facility. The chlorinolysis reactor is used to treat the contaminated wastewater in 2,000 gallon batches.  $\text{Cl}_2$  is supplied as a gas to the reactor. Control of pH is maintained by the addition of 50 percent NaOH during the chlorinolysis reaction. After the reaction is completed the excess chlorine can be stripped by nitrogen to less than 100 ppm. The residual chlorine can be neutralized with  $\text{Na}_2\text{S}_2\text{O}_3$  at this point. The pH is then adjusted to 7.0 and the reactor contents are discharged to a holding pond. This pond is sampled periodically for hydrazines and is then pumped to disposal.

The major components of the reactor system are described in detail below:

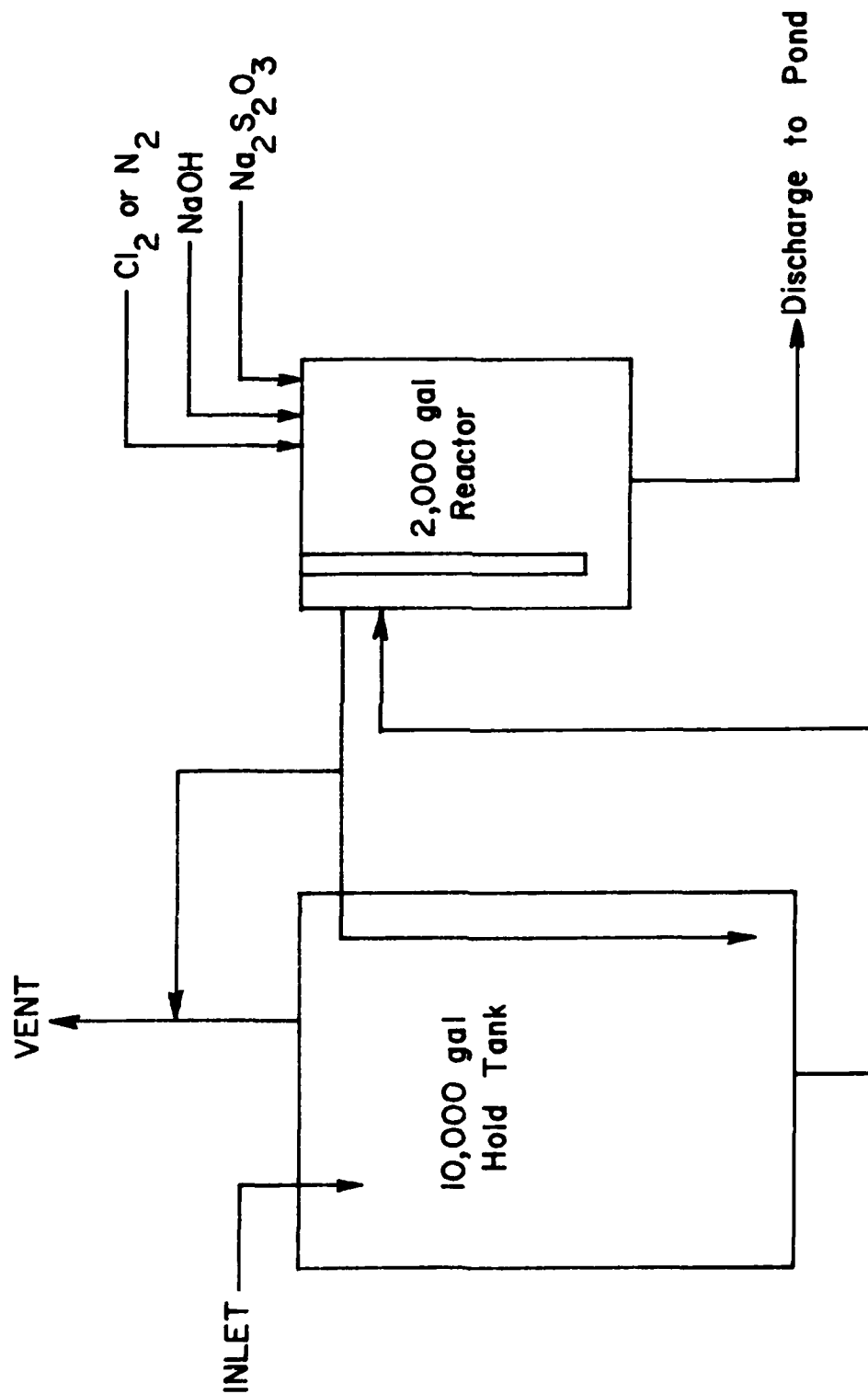


Figure 1. Process Flow Diagram UV Chlorinolysis Reaction System.

### Wastewater Hold Tank

This tank was sized at 10,000 gallons. This tank is constructed of FRP using Dow Derakane 470-36 resin. It is equipped with two sight glasses, a liquid level sight glass, a liquid level dp (differential pressure) cell connected to a high level alarm, a vent line, and a sparger which bubbles the reactor vent gases through the wastewater in the holding tank.

This tank should not be operated above 120°F nor below 40°F. The tank should never be pressurized, therefore care must be taken to ensure that the vent line is open at all times during operation. Pressure relief valves were placed in the vent system to guard against an overpressure.

### Chlorinolysis Reactor

The chlorinolysis reactor is a 2,000 gallon glass lined reactor vessel. This reactor is the heart of the treatment system. It is equipped with an agitator and a sparger to ensure good reactant mixing and contact. A UV light is immersed in the reactor to activate the chlorinolysis reaction; 7500 watts of low pressure Hg lamp UV light are required.

The pH and chlorine concentration of the reactor contents must be carefully monitored and controlled. An ORP (oxidation/reduction potential) system has been determined to be best suited for chlorine control. The pH and ORP probes are placed in an external recirculation loop. Care must be taken to ensure that an adequate flow to the probes is maintained.

This reactor will operate at atmospheric pressure, and the temperature in the reactor should not exceed 125°F. A high temperature alarm and control system is installed to prevent a temperature excursion should high concentrations of hydrazine be introduced to the reactor.

#### Nitrogen Stripping System

The same sparger system will be used for the stripping operation as for the chlorinolysis system. Only two extra valves and some extra piping are required. Compressed nitrogen is required at 30 psig and 10 ft<sup>3</sup>/min.

#### Chlorine Addition System

The chlorine addition system is controlled by the ORP instrument located in the reactor recirculation loop. Control valves are installed in the supply line to turn the chlorine flow on and off as required. The valves, piping, and sparger are the major components of this system. They are constructed of stainless steel or FRP.

#### Caustic Addition System

Control of pH is required for the chlorinolysis reaction. This requires a supply tank for the NaOH solution used to maintain pH control, a metering pump, valves and plumbing. The caustic hold tank is constructed of Dow Derakane FRP. The valves and piping can be constructed of PVC or stainless steel. The metering pump is a 1.0 gpm positive displacement metering pump.

### Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> Addition System

This system is the same size and will be constructed of the same materials as the NaOH addition system.

### Fluid Transfer Pumps

One reactor recirculation pump and two fluid transfer pumps are required. The recirculation pump must supply 15 gpm through the instrumentation loop. Two 40 gpm fluid transfer pumps are required to fill and empty the reactor. All three pumps will be constructed of FRP with a vinyl ester resin and will have double mechanical seals to prevent wastewater leakage into the operating area.

### Vent Systems

It was decided to vent the chlorinolysis reactor to the hold tank during the chlorinolysis reaction. Instead of nitrogen stripping, the reaction may be allowed to sit for several hours with the UV light on and the chlorine supply off. UV will decompose the residual chlorine to HCl. The rate of this reaction is unknown, but is believed to be sufficient to avoid the stripping procedure. Experimental work to test the feasibility of UV for chlorine removal was not performed and will be tested at the actual installation.

### Instrumentation

The instrumentation for the process consists of a pH control system for the chlorinolysis reactor, and an ORP system which is

used to control the chlorine flow to the reactor and to monitor the chlorine neutralization with  $\text{Na}_2\text{S}_2\text{O}_3$ . Liquid level indicators and controllers were provided for the hold tank and reactor. In addition, a temperature alarm system was included to guard against severe exothermic reactions which could occur if very concentrated hydrazines were fed to the reactor.

#### Quality of the Treated Wastewater

Samples of the chlorinolysis and the UV chlorinolysis reaction products were analyzed for chlorinated hydrocarbons and chloramines since these compounds could be formed by the chlorinolysis of  $\text{NH}_3$ ,  $\text{CH}_4$ , or  $\text{CH}_3\text{OH}$ . These three compounds are possible side products of the reaction of Hz, MMH, UDMH, and DMNA with chlorine.  $\text{CH}_3\text{OH}$ , in particular, is expected to be a primary reaction product of the chlorinolysis of both MMH and UDMH.

If these compounds react with chlorine they could form:  $\text{CH}_3\text{Cl}$ ,  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$ ,  $\text{CCl}_4$ ,  $\text{NH}_2\text{Cl}$ ,  $\text{NHCl}_2$  and  $\text{NCl}_3$ .  $\text{NCl}_3$  is the most undesirable of these since it is explosive. The other components are all toxic and therefore, it was of interest to know how much of each of these components would be formed.

Samples of the end products of pilot reactions #1 and #2 and the end products of UV chlorinolysis were analyzed and results are shown in Table 1. Significant amounts of chlorinated contaminants remained in the treated wastewater from the pilot plant chlorinolysis reactions. However, no contaminants were found in the end

product of the UV chlorinolysis experiment. This illustrates that UV chlorinolysis possesses a distinct advantage over low pH chlorinolysis in that it produces a much cleaner effluent.

The same three solutions were tested for the presence of  $\text{NH}_2\text{Cl}$ ,  $\text{NHCl}_2$  and  $\text{NCl}_3$ . These tests were expected to be negative since the  $\text{Na}_2\text{S}_2\text{O}_3$  used for neutralization of  $\text{Cl}$  was expected to readily react with all three compounds. None of these compounds were detected.

TABLE 1. CHLORINOLYSIS END PRODUCT ANALYSIS

	Concentration, ppm				Unk. #465
	<u><math>\text{CH}_3\text{Cl}</math></u>	<u><math>\text{CH}_2\text{Cl}_2</math></u>	<u><math>\text{CHCl}_3</math></u>	<u><math>\text{CCl}_4</math></u>	
Pilot Plant Run #1 end product	1-2	0	10.71	6.3	15
Pilot Plant Run #2	0	0	5.3	1.8	5
UV Chlorinolysis end product (10/6/78)	0	0	0	0	0
Initial Concentrations, ppm					
	<u>H<sub>2</sub></u>	<u>UDMH</u>	<u>MMH</u>	<u>DMNA</u>	
Run #1		1000	1000	1000	100
Run #2		500	500	500	100
UV/ $\text{Cl}_2$		0	0	0	0

An additional experiment was performed to test for the presence of these compounds during a low pH chlorinolysis experiment. This was expected to be a worst case situation. Results are shown in Table 2.

### BOD Toxicity Tests

The chlorinolysis reactor effluent may contain some chlorinated hydrocarbons or amines which will have a harmful effect on a biological wastewater treatment system. The toxicity of this effluent stream was studied using 5 and 20 day BOD procedure.

The water from the low pH chlorinolysis experiment exhibited no noticeable toxicity. The water from the UV chlorinolysis run appeared to inhibit biological growth for 1-5 days but was not toxic.

TABLE 2. CHLORINOLYSIS END PRODUCT ANALYSIS  
FOR CHLORINATED AMINES

	<u>Concentration, ppm</u>			
	<u>Cl</u>	<u>NH<sub>2</sub>Cl</u>	<u>NHCl<sub>2</sub></u>	<u>NCl<sub>3</sub></u>
Low pH Chlorinolysis Experiment				
15 min	997	16.7	59.9	0
60 min	972	0	0	0
105 min	910	0	0	0
150 min	868	0	0	0
<u>Initial Concentrations</u>				
Hz 2000 ppm				
UDMH 2000 ppm				
MMH 2000 ppm				

Note: 0 = <.1ppm

### Current Status

This wastewater treatment process is being considered for the treatment of wastewater from the Air Force hydrazine blending facility located at Rocky Mountain Arsenal and may have application at other facilities.

### Acknowledgement

This work was conducted as a part of Air Force Contract No. F 04611-76-C-0043.

PAPER NO. 9

ESTIMATION OF HAZARD CORRIDORS  
FOR SPILLS OF HYDRAZINE BASED FUELS

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Introduction

Due to their excellent propellant properties, amine-based fuels are being used in a growing number of Air Force systems. Aerozine 50, a 1:1 mixture of hydrazine (Hz) and unsymmetrical dimethylhydrazine (UDMH), is employed in the Titan missile. The space shuttle requires both hydrazine and monomethylhydrazine (MMH) for various aspects of its mission. But perhaps the most widespread use of hydrazine has resulted from its use in the Emergency Power Unit (EPU) on the F-16 general purpose fighter in the form of a 70 percent solution of hydrazine in water (H-70). The expanded use of these highly energetic but toxic liquid fuels creates an increased potential for accidental spills. In the event of such a spill, steps must be taken to protect nearby personnel from exposure to hazardous vapor concentrations. The recent identification of hydrazine as a suspected carcinogen makes this need particularly acute. Protection of personnel is generally

accomplished by defining a hazard corridor within which exposure levels are considered to be unacceptable. Personnel are then withdrawn from the hazard corridor area unless they are wearing suitable protective equipment. Estimating the most likely size of the hazard corridor for a given scenario must generally be accomplished prior to any operations involving toxic materials to limit the possibility of unnecessary exposure. An example of a calculated hazard corridor is shown in Figure 1. This example, which is taken from Reference 1, shows the predicted distance to the  $7 \text{ mg/m}^3$  short term public exposure limit for three hydrazine spill volumes.

Following the spill of a liquid material onto the ground, the liquid will evaporate at a rate which depends primarily on the liquid's volatility, the temperature, the exposed surface area, and the level of wind generated turbulence. The vapor thus produced is carried downwind and dispersed by molecular and eddy diffusion processes. Therefore, the determination of a hazard corridor involves two separate calculations. First an estimate of the evaporation rate or "source strength" must be made. Second an atmospheric dispersion model must be employed to predict the distance required to dilute that source strength to a concentration judged to be tolerable. For both of these steps there are several options presently available. Choice of the best method for a given situation depends upon the nature of the spill, the accuracy required, the computational facilities available, and the meteorological data which can be obtained.

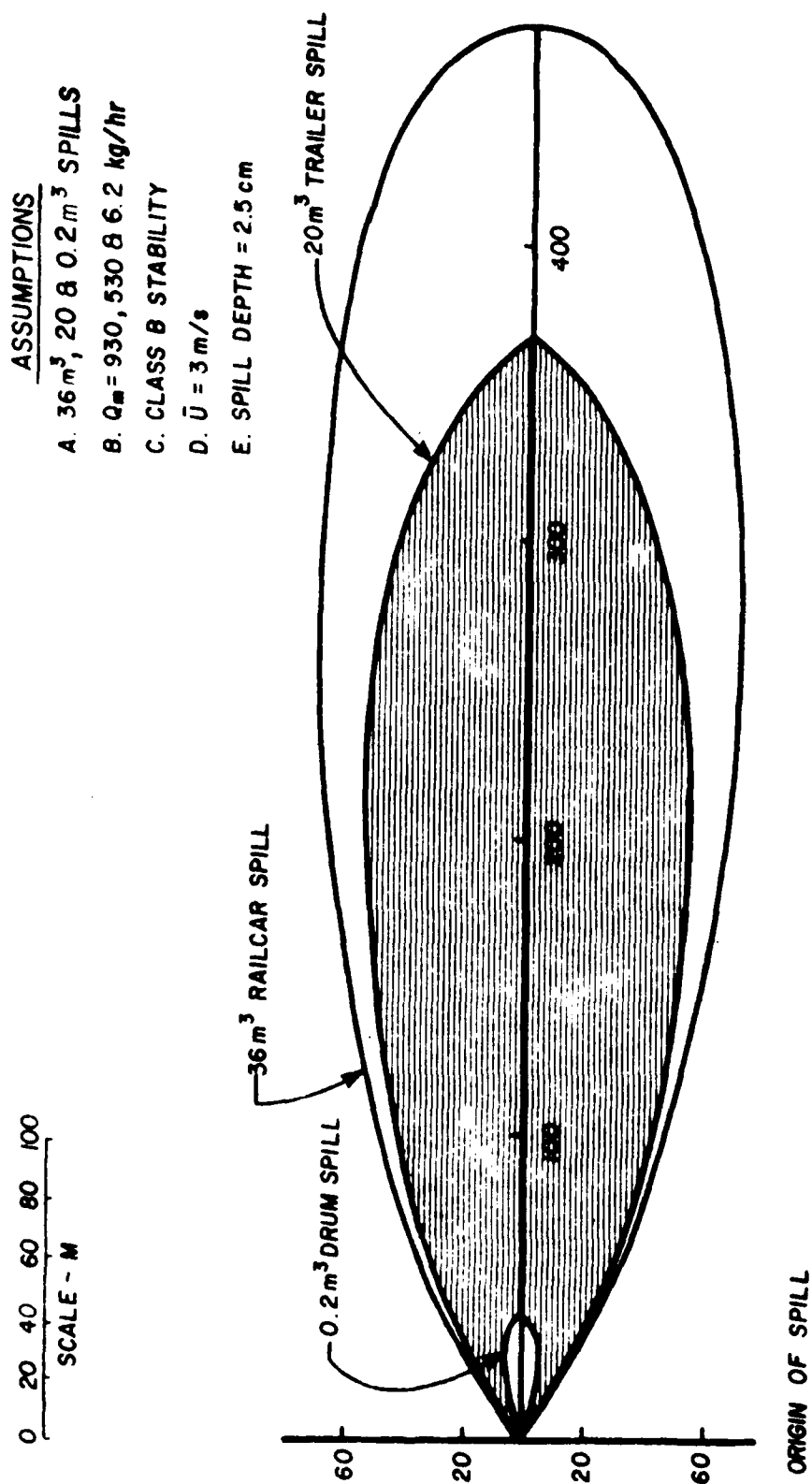


Figure 1. Illustration of the 7 mg/m<sup>3</sup> Short-Term Public Limit Hazard Corridor for Hydrazine.

### Source Strength Estimation

In some cases written guidelines have been prepared giving potential source strengths for selected spill scenarios. The Strategic Air Command, for example, has provided its Titan II units with suggested source strengths for spills or leaks during various propellant system operations (Reference 2). Such guidelines are particularly necessary where the source strength is primarily determined by a liquid leak rate or where enclosure of the spill, such as in a missile silo, makes the application of an evaporation model difficult.

Where guidelines are not available, the rate of evaporation must be calculated from a computer model or semi-empirical formula. The Engineering and Services Laboratory (ESL) has developed a computer model of evaporation from ground spills specifically for the hydrazine based fuels. The report on this model (Reference 1) contains several graphs which can be used to rapidly estimate source strengths for large spills. One of these graphs is reproduced as Figure 2 and shows, for example, that a 200 liter hydrazine spill at a temperature of 30°C produces a source strength of slightly over 10 kg/hr.

Alternatively the computer model itself can be run for the specific case in question. If computer facilities are not available, the program can be run by ESL upon request. Due to the calculation of the steady state temperature of the evaporating pool based on solar insolation, conduction from the air and

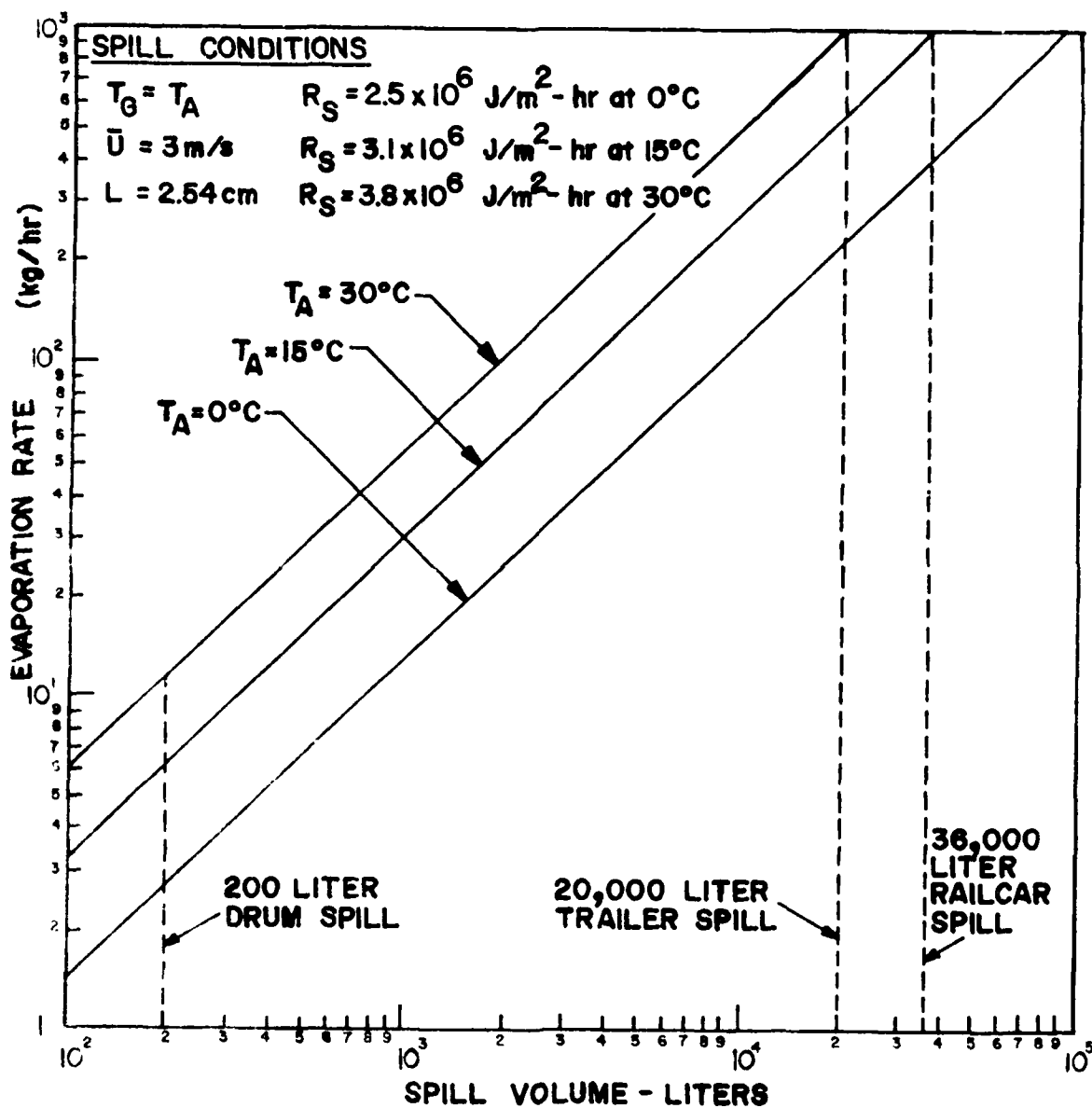


Figure 2. Hydrazine Propellant Evaporation Rates as a Function of Ambient Air Temperature and Spill Volume.

ground, radiative emission, and evaporative cooling, the model is too complicated to program on a hand-held calculator. A similar model which can be programmed on a hand-held calculator has been developed by the Army (Reference 3). This model simplifies the calculation by assuming the pool temperature is equal to the air temperature. However, since the Army model was designed for use with chemical warfare agents, its application to propellant spills requires the user to input several propellant properties: the vapor pressure at the pool temperature, the molecular weight, and the molar volume at the propellant boiling point.

Due to the difficulties involved in using computer or calculator programs in a field situations, it is desirable to have a simple formula which can provide a rough estimate of source strengths based on a minimum of input parameters. The Air Weather Service has published an empirical equation, based on laboratory studies of  $N_2O_4$ , which can be used to estimate source strengths for highly volatile liquids such as UDMH (Reference 4):

$$Q = 18.7 U^{0.8} A \quad (1)$$

where  $Q$  = source strength (kg/hr)

$U$  = wind speed (m/s)

$A$  = spill area ( $m^2$ )

Other than the fact that rigorously this equation applies only to  $N_2O_4$ , its most obvious limitation is the lack of an explicit tem-

perature dependence. However, the ESL evaporation model can be written in a similar form:

$$Q = 0.0292 S_c^{-0.67} U^{0.78} X^{-0.11} A P_v M / R T_p \quad (2)$$

where  $S_c$  = the Schmidt number for the system

$X$  = the pool downwind diameter

$P_v$  = the propellant vapor pressure

$M$  = the propellant molecular weight

$R$  = the universal gas constant

$T_p$  = the temperature of the pool and the exponents of  $U$  and  $X$  correspond to a typical ground roughness of 2.5

Ignoring the relatively small effect of the Schmidt number and the downwind diameter and recognizing that the vapor pressure,  $P_v$ , is a direct function of the pool temperature,  $T_p$ , we can simplify the above equation and obtain the following approximation:

$$Q = C U^{3/4} A f(T_p) \quad (3)$$

In this equation  $f(T_p)$  is a function of the pool temperature which can be determined empirically along with the constant  $C$ .

Figure 3 shows that the predictions of the ESL model for hydrazine spills can be fit quite well for the temperature regime  $0 < T_p(^{\circ}C) < 50$  by assuming a second order dependence on temperature as expressed in the following formula:

$$Q = 0.08 U^{3/4} A (1 + 4.3 \times 10^{-3} T_p^2) Z \quad (4)$$

where the added factor Z is discussed below.

In order to apply this formula to compounds other than hydrazine, the factor Z can be determined which represents the ratio of the vapor pressures and molecular weights of hydrazine and the desired compound. Figure 4 shows the vapor pressure of several propellants and oxidizers in the temperature regime of interest. From this graph the ratio of vapor pressures can be determined. The factor Z is then simply:

$$Z = \frac{P_{vB}}{P_{vH}} \frac{M_B}{M_H} \quad (5)$$

where  $P_{vB}/P_{vH}$  = the ratio of the vapor pressure of the desired compound to that of hydrazine at the same temperature.

$M_B$  = the molecular weight of the desired compound

$M_H$  = the molecular weight of hydrazine = 32

Table 1 shows the values of Z for several propellants and oxidizers. In the case of MMH and UDMH, Z can also be calculated by comparison of the predictions of equation 4 with the ESL model results from MMH and UDMH in Reference 1. The values of Z calculated in this way agree within three percent with those in Table 1. Also, although the temperature at which equation 1 was empirically derived is not known, for typical experimental temperatures of 15°C to 20°C the value of Z for  $N_2O_4$  based on laboratory studies

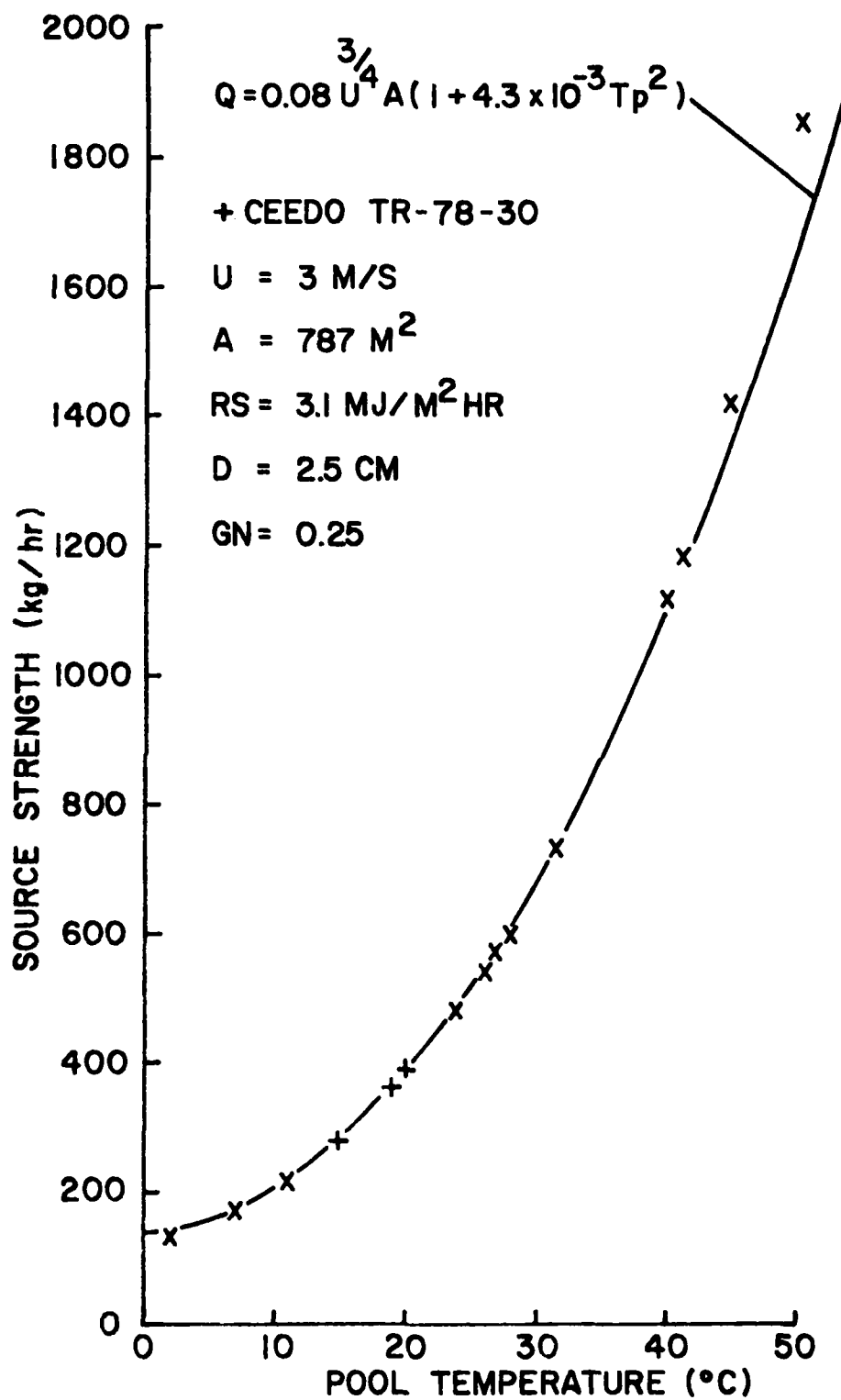


Figure 3. Comparison of Source Strength Predictions of a Simple Formula with those of a Computer Evaporation Model.

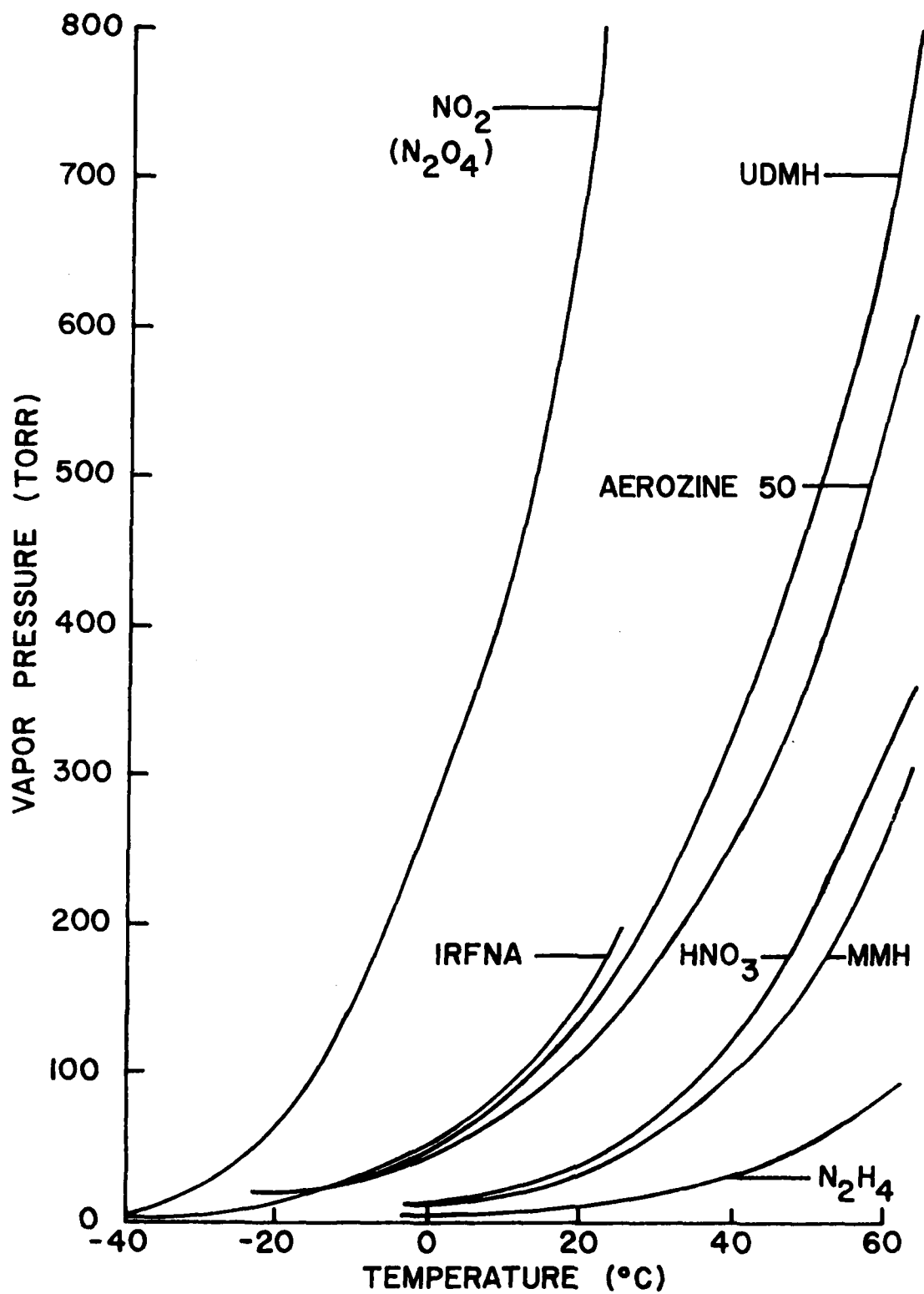


Figure 4. Vapor Pressure of Selected Propellants.

would fall between 80 and 120, again in good agreement with Table 1.

TABLE 1. SOURCE STRENGTH FACTORS RELATIVE TO HYDRAZINE

Compound	$\frac{P_{VB1}}{P_{VH}}$	$M_B$	Z
Hydrazine	1	32.0	1
MMH	3	46.1	4.3
Aerozine 50	10	53	16.6
UDMH	11	60.1	20.7
IRFNA	12 <sup>2</sup>	60.5 <sup>2</sup>	22.7
N <sub>2</sub> O <sub>4</sub>	70 <sup>3</sup>	46.0 <sup>3</sup>	100

1. Average value from Figure 4 for  $0 < T_p (C) < 50$
2. Estimated, based on 15 percent NO<sub>2</sub>, 85 percent HNO<sub>3</sub>
3. As NO<sub>2</sub>

The most difficult aspect of applying equation 4 is estimating the liquid pool temperature. The ESL model predicts that for similar meteorological and spill conditions, the evaporation rates of MMH and UDMH are three and eleven times that of hydrazine, respectively (Reference 1). The difference between these factors and the corresponding values in Table 1 is due to the greater evaporative cooling effect produced by the more volatile compounds. For example, under identical spill conditions a pool of UDMH will become more than 10°C cooler than a pool of hydrazine due to its higher evaporation rate. Other parameters which affect the pool temperature include the temperature of the air and the ground and

the heating effect of solar insolation. Most models assume the pool temperature to be equal to the air temperature; however, Reference 1 shows that this assumption can lead to substantial error. Nevertheless, the air temperature provides the easiest and most likely estimate of the pool temperature under most conditions. For very sunny conditions, the pool temperature should be chosen 10°C to 20°C above the air temperature. For highly volatile compounds the pool temperature can be lowered by 10°C to 20°C to allow for evaporative cooling.

Figure 5 shows a comparison of model predictions with experimental data obtained in our laboratory (Reference 5). The actual evaporation rate decreases with time due to reactions with atmospheric water and carbon dioxide, so bars were chosen to represent typical mass flux rates between twenty and sixty minutes after a spill. Although the data was obtained for small spills in fume hoods, the rates are considered to be fairly representative of real situations. The temperature shown is the temperature of the pool ( $T_p$ ). Pool temperatures above 30°C were obtained by raising the ground temperature ( $T_g$ ) while leaving the air temperature ( $T_a$ ) at ambient. All MMH trials were run at 24°C with  $T_a = T_g$ . Both the Air Force and Army models tend to over-predict evaporation rates when  $T_g = T_a$ , however, for  $T_g$  greater than  $T_a$  (as on a sunny day) the Army model falls behind the Air Force model since it assumes  $T_p = T_a$ . The simple formula predicts close to the first hour average rate when the actual pool temperature is used. The reason it differs from the Air Force model on which it

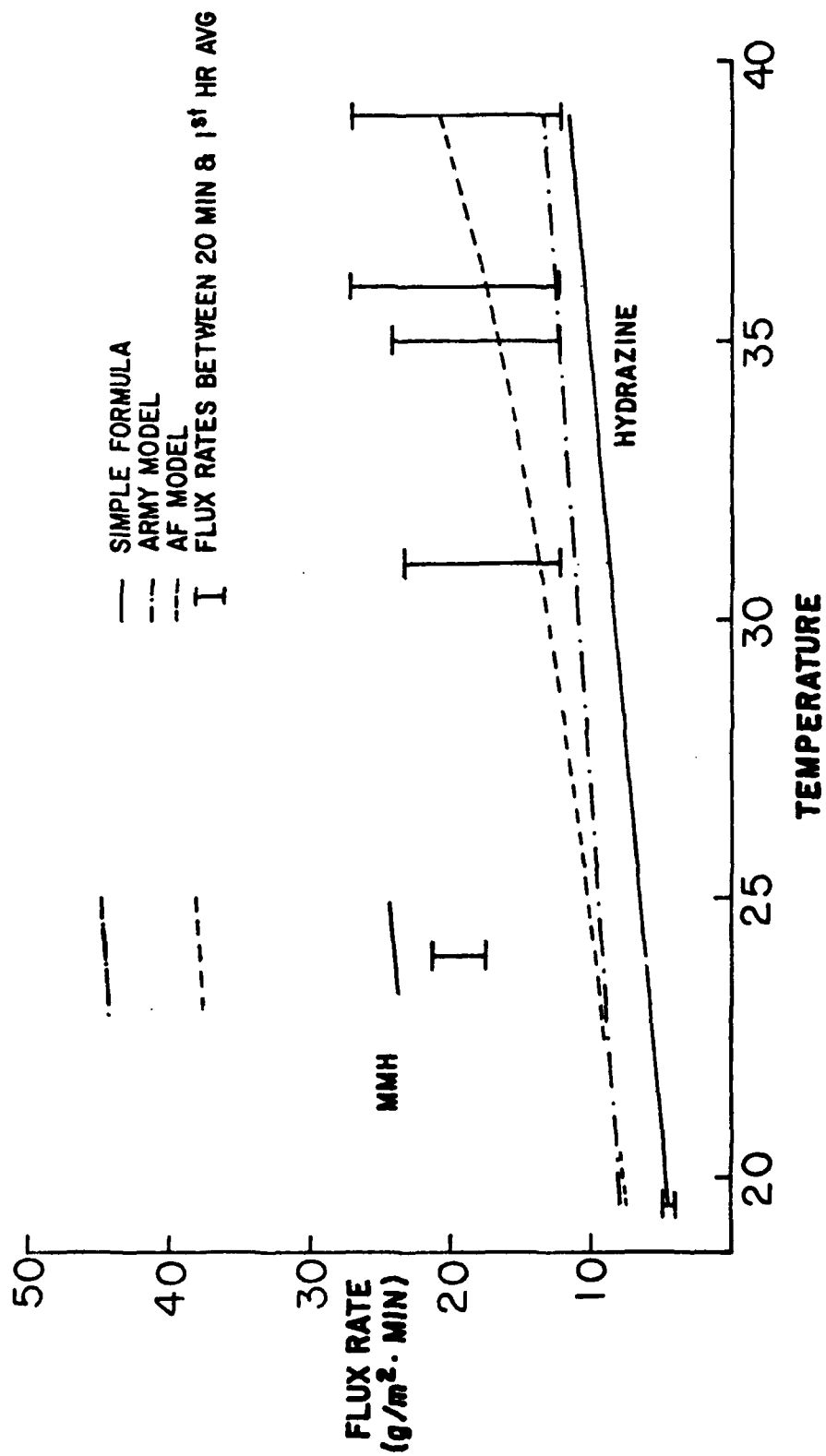


Figure 5. Comparison of Evaporation Models with Experimental Data

is based is because the experimental pool area is well outside the region in which the formula was derived, and the evaporation rate shows a weak dependence on pool diameter not included in the formula. At any rate the rough agreement of all the models with the experimental data is encouraging.

#### Hazard Corridor Determination

Once the evaporation rate (source strength) from a spill has been determined, an atmospheric dispersion model can be used to determine the dimensions of the hazard corridor. Certainly the most popular type of dispersion model in use today is the "Gaussian" model. Reference 6 provides an excellent introduction into the use of this type of model along with example problems and reference graphs. For the fast solution of problems in the field, however, a dispersion estimate can be more quickly made using the graphs in Reference 1. One of these graphs is reproduced as Figure 6. Curves A through F correspond to the atmospheric stability categories defined in Figure 7 (Reference 6). Moving across from a source strength of 100 kg/hr, the curve for neutral stability, D, is intersected at a distance of 400 meters. This distance defines the downwind hazard corridor dimension to the short term public exposure limit for hydrazine ( $7 \text{ mg/m}^3$ ). For other downwind concentrations, the source strength is modified according to the formula:

$$Q_2 = Q_1 (C_1/C_2) \quad (6)$$

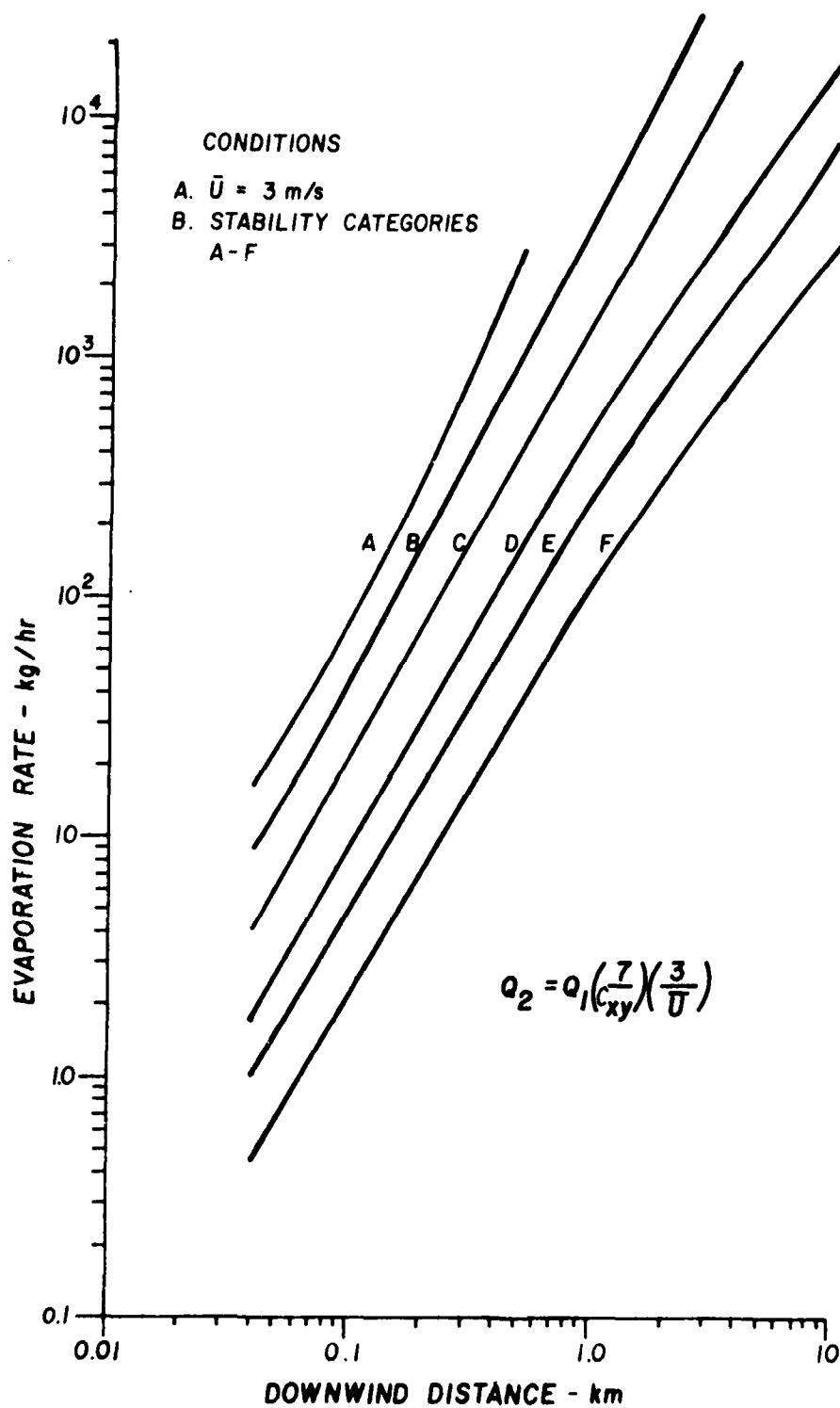


Figure 6. Downwind Evacuation Distance to the Short-Term Public Exposure Limit Concentration for Hydrazine.

# ESTIMATED ATMOSPHERIC STABILITY CATEGORIES (TURNER)

U (m/s)	Day			Night	
	Incoming Solar Radiation			Thinly overcast or ≥ 4/8 low clouds	≤ 3/8 low clouds
	Strong	Moderate	Slight		
2	A	A-B	B		
2-3	A-B	B	C	E	F
3-5	B	B-C	C	D	E
5-6	C	C-D	D	D	D
6	C	D	D	D	D

The neutral class, D, should be assumed for overcast conditions during day or night, regardless of wind speed.

A - most unstable  
D - neutral  
F - most stable

## Insolation:

Strong - solar altitude  $>60^\circ$  clear skies

Slight - solar altitude  $15-35^\circ$  , clear skies

Strong insolation with broken (5/8-7/8) middle clouds is reduced to moderate

Strong insolation with broken low clouds is reduced to slight

Night lasts from one hour before sunset till one hour after sunrise

---

Taken from Turner's "Workbook of Atmospheric Dispersion Estimates", 1970, EPA Publication # AP-26

Figure 7. Estimated Atmospheric Stability Categories (from reference 6).

where  $Q_2$  = the source strength to be used with the graph

$Q_1$  = the actual source strength

$C_1$  = the downwind concentration used in the graph  
(in this case  $7 \text{ mg/m}^3$ )

$C_2$  = the selected downwind concentration

Another model in common use to predict atmospheric dispersion is the "Ocean Breeze/Dry Gulch" model developed by the Air Force Geophysics Laboratory. This model is sometimes referred to as the "Delta T" model since it requires the input of the difference in temperature between 54 feet and 6 feet above the ground.

Figure 8 (Reference 4) can be used to estimate this difference if it is not available from a measurement tower. A typical chart from Reference 4 is shown as Figure 9. To obtain the distance to the 30 minute public exposure limit for hydrazine (20 ppm), read across from the source strength in pounds per minute to the column for the appropriate Delta T. The entry there gives the downwind hazard distance in feet. Once again equation (6) can be used to obtain different downwind concentration limits.

A comparison of the two models just described is shown in Figure 10. The points shown represent the predictions of both models for a variety of cases including source strengths from 30 to 80,000 kg/hr and atmospheric conditions ranging from stable to unstable (as determined from Figures 7 and 8). The solid line represents

ESTIMATION OF TEMPERATURE DIFFERENTIAL °F (54-6 FT ΔT)  
(In rough terrain add (-1) to the number determined)

DAY										NIGHT					
SURFACE WIND SPEED (kt.)	INCOMING SOLAR RADIATION										CLEAR	CLOUD COVER 1/8-3/8		CLOUD COVER 4/8-8/8	
	STRONG (≥ 60)	(SOLAR ELEVATION ANGLE)				WEAK (16-35°)		*SUNRISE/SUNSET ( $\leq 15^\circ$ )		NO SNOW		NO SNOW	NO SNOW	NO SNOW	
		MODERATE (36-60°)	CLEAR SKY OR SCATTERED CLOUDS			MODERATE (16-35°)	WEAK ( $\leq 15^\circ$ )								
≤ 3	-2	-1	-1	-1	-1	0	0	6	5	5	4	4	3		
4-6	-3	-2	-2	-2	-2	0	0	6	5	5	4	4	3		
7-10	-3	-2	-2	-2	-2	0	0	5	4	4	3	3	2		
≥ 11	-2	-1	-1	-1	-1	0	0	5	4	4	3	2	1		
BROKEN CLOUDS EQUAL TO 6 BLO 7000 FT - A (>) TO 6 BLO 7000 FT - B (≤)															
	A	B	A	B	A	B	A	B	A	B					
≤ 3	-1	-1	-1	-1	-1	0	0	0	0	0					
4-6	-2	-2	-2	-2	-2	0	0	0	0	0					
7-10	-2	-1	-1	-1	-1	0	0	0	0	0					
≥ 11	-1	-1	-1	-1	-1	0	0	0	0	0					
OVERCAST CLOUDS															
≤ 3	-1	0	-1	0	-1	0	-1	0	0	0					
4-6	-2	0	-2	0	-2	0	-2	0	0	0					
7-10	-1	0	-1	0	-1	0	-1	0	0	0					
≥ 11	-1	0	-1	0	-1	0	-1	0	0	0					

\*Use sunrise/sunset category during the period from one hour before to one hour after sunrise/sunset.

\*Use sunrise/sunset category during the period from one hour before to one hour after sunrise/sunset.

NOTE: "Estimation of Temperature Differential" was prepared by Maj Robert G. Curry while assigned to 3AW/DN. Credit for the work in this pamphlet goes to many people. Maj Curry and Capt Raymond Kandier, 3AW/DN, brought it to fruition. The information originally appeared as 3AWP 105-13.

Figure 8. Estimation of Temperature Differential (from reference 4).

# HYDRAZINE

SS L47414	DELTA T (DEG F)									
	-4	-3	-2	-1	0	1	2	3	4	5
1.0	152	154	213	297	375	477	595	729	879	1046
5.0	215	347	487	656	850	1090	1356	1663	2006	2388
10.0	330	490	695	930	1222	1555	1938	2373	2863	3408
15.0	413	613	855	1152	1504	1915	2386	2922	3524	4197
20.0	479	717	991	1330	1744	2219	2766	3386	4085	4864
30.0	590	871	1221	1645	2147	2732	3425	4169	5029	5988
40.0	643	1004	1415	1916	2488	3167	3947	4833	5829	6941
50.0	760	1132	1596	2137	2794	3551	4425	5419	6536	7783
75.0	943	1393	1953	2631	3435	4372	5449	6672	8047	9582
100.0	1093	1615	2264	3054	3981	5067	6315	7732	9327	11106
150.0	1391	2055	2991	3991	5067	6449	8037	9891	11870	14134
200.0	1921	2937	3978	5358	6995	8903	11095	13586	16307	19513
300.0	2726	3288	4610	6211	8188	10319	12868	15746	18993	22627
500.0	2497	3687	5169	6964	9291	11578	14419	17656	21297	25359
750.0	3074	4544	6365	8574	11193	14245	17753	21738	26221	31222
1000.0	3563	5252	7377	9937	12973	16511	20576	25195	30391	36107
2000.0	5144	7547	10527	14181	18513	23561	29363	35954	43368	51639
3000.0	6259	9245	12961	17450	22793	29009	36152	44267	53306	63579

HAZARD CORRIDOR LENGTHS IN FEET FOR VARIOUS SOURCE STRENGTHS IN LB/MIN  
20.2PPM 30 Minute PEL  
HYDRAZINE

Figure 9. Hazard Corridor Lengths for Hydrazine 30-Minute PEL (from reference 4).

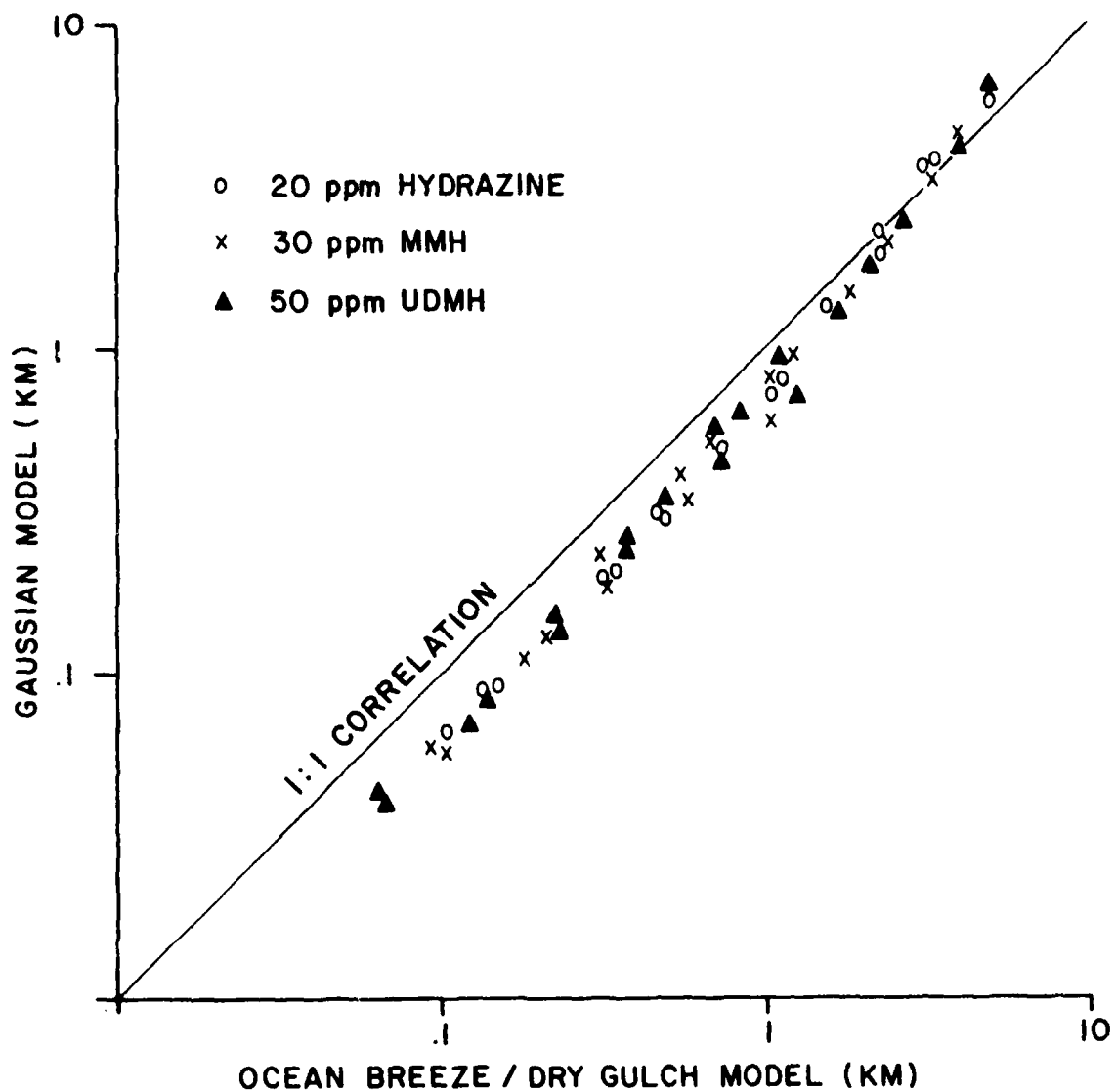


Figure 10. Correlation of Predicted Hazard Corridor Lengths for a Variety of Source Strengths and Stabilities

exact agreement. The two models correlate quite well, although the Ocean Breeze/Dry Gulch model appears to become more conservative at shorter distances. In all cases the predictions of the two models are within a factor of two or less. Thus the choice of dispersion model is best dictated by the availability of input parameters and ease of application in a given situation.

The width of the hazard corridor can be estimated either from the dispersion model (Reference 1) or from the measured wind variability (Reference 4). However, short term fluctuations in wind direction can often exceed expected variability by a large margin. Therefore, particularly under light and variable wind conditions, it might be prudent to consider the cordoned area to be a circle with radius equal to the downwind hazard distance.

#### Example Calculations

Example 1: 20,000 liter hydrazine spill

air temperature: 15°C (60°F)

wind speed: 3m/s (6 knots)

weather: mostly sunny

If the spill area is not known it can be estimated, for large spills on uneven ground, by assuming the average depth is roughly 2.5 cm (1 inch). This yields an area for the present case of 800 m<sup>2</sup>.

Source Strength:

- a. From Figure 2 (Reference 1):  $Q = 530 \text{ kg/hr}$
- b. From equation 4, assuming the pool temperature is  $10^\circ\text{C}$  above the air temperature due to the sunny conditions:

$$Q = 0.08(3)^{3/4}(800)(1+4.3 \times 10^{-3}(25)^2) = 540 \text{ kg/hr}$$

Downwind hazard corridor distance to short-term public exposure limit ( $7 \text{ mg/m}^3$ ):

a. From Figure 7, for moderate to strong solar insolation and 3 m/s winds, the stability category is probably B. Then from Figure 6, for an evaporation rate of 540 kg/hr and stability category B, the downwind hazard distance is 370 meters.

b. From Figure 8 the temperature difference is probably  $-2^\circ\text{F}$ . To use Figure 9 with a concentration of  $7 \text{ mg/m}^3$ , the source strength of 540 kg/hr (20 pounds per minute) must be adjusted using equation 6. Since 1 ppm of hydrazine is equivalent to  $1.3 \text{ mg/m}^3$ ,  $Q_2 = 20 [20 \times (1.3) / 7] = 75 \text{ pounds per minute}$ . Then from Figure 9, for a source strength of 75 and a Delta T of  $-2^\circ\text{F}$ , the hazard corridor length is 1953 feet (600 meters).

(The hazard corridor for this example is illustrated by the shaded area in Figure 1).

Example 2: 5 liter spill of H-70

air temperature: 21°C (70°F)

wind speed: 3 m/s (6 knots)

weather: heavily overcast

For small spill volumes on a flat concrete surface, the average spill area can be estimated as 2 m<sup>2</sup>/liter. Thus in this example the spill would cover an area of approximately 10 m<sup>2</sup>.

Source strength: Experimental studies in our laboratory have shown that the rate of evaporation of 70 percent hydrazine in water is approximately one-third that of pure hydrazine. Therefore letting  $Z = 1/3$  in equation 4:

$$Q = 0.08(3)^{3/4}(10)(1+4.3 \times 10^{-3}(21)^2)^{1/3} = 1.76 \text{ kg/hr}$$

Downwind hazard corridor length to the threshold limit value maximum possible permissible excursion level (0.3 ppm or 0.39 mg/m<sup>3</sup>):

a. From equation 6,  $Q_2 = 1.76 (7/0.39) = 31.6 \text{ kg/hr}$ .

Overcast conditions indicate stability class D. Then from Figure 6 the downwind hazard distance is approximately 210 meters.

b. From equation 6,

$$Q_2 = 1.76 (20/0.3) = 117 \text{ kg/hr} = 4.3 \text{ lbs per min}$$

From Figure 8 Delta T is probably 0°F. Then from Figure 9, for a source strength of 5 pounds per minute and a Delta T of 0°F, the hazard corridor length is 856 feet (260 meters).

## Summary

The estimation of a downwind hazard corridor distance for a liquid spill is most easily addressed in two steps. In the first step, the evaporation rate of the liquid must be determined. If source strength guidelines are not available for a particular case the evaporation rate can be estimated by using an evaporation model. A simple, semi-empirical formula for rapid field estimation of source strengths has been derived (equation 4) which gives good agreement with the predictions of more complicated computer models as well as with experimental results for hydrazine, MMH, and nitrogen tetroxide. In the second step, the distance required for atmospheric diffusion to reduce vapor concentrations below a hazardous level must be computed. A comparison of diffusion estimates using the Air Force Ocean Breeze/Dry Gulch model versus a standard Gaussian model shows good agreement for a variety of source strengths and atmospheric stabilities. Thus the choice of a diffusion model should be based on availability of required input parameters and ease of application for the particular case.

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PAPER NO. 10

DETERMINATION OF ENVIRONMENTAL PHYSICAL-  
CHEMICAL PROPERTIES OF HYDRAZINE

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Introduction

To accurately assess the environmental fate and impact of hydrazine fuel usage (hydrazine, Hz; monomethylhydrazine, MMH; and unsymmetrical dimethylhydrazine, UDMH) the physical and chemical behavior of these fuels in the environment must be determined. The Environmental Sciences Division of AFESC is conducting such studies in three general areas: (a) determination of evaporation rates of spilled fuels, (b) determination of decomposition rates in atmospheric, aquatic, and terrestrial phases, and (c) identification of decomposition products formed in these studies. This paper summarizes our work to date.

### Materials and Methods

Reagents: All chemicals were ACS grade or better except for the hydrazine fuels. Hydrazines were Air Force fuel grade and used as obtained from Rocky Mountain Arsenal.

Analytical Methods: Non-specific hydrazine fuel concentrations were assayed by potassium iodate titration (reference 1). Specific hydrazine species were quantitated by either colorimetry or pyrazole derivative gas chromatography (reference 2). Colorimetric analyses were performed with paradimethylaminobenzaldehyde (PDAB) method (reference 3) for Hz and MMH, and with trisodium pentacyanoaminoferroate (TPF) method (reference 4) for UDMH.

Fourier transform long path infrared spectroscopy was utilized for the atmospheric hydrazine decompositions. Decomposition products were also identified through gas chromatography/mass spectrometry.

### Experimental Procedures

Evaporation Study: Fuel evaporation rates were determined under controlled laboratory conditions in glass dishes of various sizes (11.6, 63.6, and 177 cm<sup>2</sup>). Air velocity over the evaporating surface of the fuel was 132 cm/sec and the relative humidity ranged from 65-85 percent. Temperature of the evaporating fuel was controlled ( $\pm 2^{\circ}\text{C}$ ) with a sand bath in a thermostated water bath. Fuel temperatures ranged from 20° to 40°C. Initially a known volume of fuel was weighed in a glass dish; then at time intervals throughout the experiment the dish was re-weighed and microliter

quantities of fuel were removed for compositional analysis. The evaporative fuel loss was not corrected for this small analytical loss.

**Aqueous Degradation:** These studies were performed with gentle mixing in closed pyrex reaction vessels to prevent evaporative losses. Decomposition rates were determined in deionized distilled water and locally obtained pond and marine waters which were filtered immediately before use. Analytical samples were withdrawn daily for both colorimetric and gas chromatographic/mass spectrometric fuel assays.

**Atmospheric Degradation:** Vapor phase decompositions of hydrazines were studied by Fourier transform long path infrared spectroscopy. The long path reaction cell was constructed of 0.152 meter by 3.05 meter Pyrex® pipe. Three mirror White-type multiple pass optics were installed in Plexiglass® mounts in the cell at a 2.75 meter separation and coupled to a Digilab Model FTS-20 Fourier Transform Infrared Spectrophotometer. The cell was operated at 72 passes during these studies for a path length of 200 meters. Spectra were recorded at  $1.0\text{ cm}^{-1}$  resolution using 64 co-added scans and triangular apodization.

A measured amount of fuel was introduced into the evacuated long path cell via an attached vacuum manifold, either by syringe injection through a silicon septum or by flushing the contents of an attached glass sample bulb. Helium was then added to adjust the total pressure to 610 Torr and the system allowed to stabilize

for 40 minutes. After the initial fuel spectrum was recorded, oxygen was added to 760 Torr total pressure and the FT-IR spectrophotometer set to automatically acquire spectra every 60 minutes. The reaction was typically followed for five hours after which a final spectrum was recorded in about 22 hours the next day. These spectra were then plotted, and hydrazine fuel concentration versus time plots were calculated.

### Results

#### Evaporation Rates:

The environmental evaporation rate of a spilled liquid is a complex function of ambient air temperature, wind speed, solar radiation, size and dimension of the spill, vapor pressure, and diffusion co-efficients. The evaporation rates of the three hydrazine fuels as measured under controlled laboratory conditions are shown in Table 1. These data, are at best, estimates of the real environmental situation since rarely would all the necessary model input parameters be available for expeditious use of a model nor would the circumstances be the same as in the laboratory study. The data show an order of magnitude difference between the evaporation of hydrazine and UDMH, which reflects the large difference in their respective vapor pressures.

The effect of surface area on the rate of evaporation was approached using water as a model liquid. The liquid volume required and laboratory safety considerations precluded using the

hydrazine fuels themselves as the study was extended to areas of 1180 cm<sup>2</sup>. To express evaporation data from pools of different surface area the data are calculated in terms of mass flux (mass of liquid evaporating per minute per area, mg/cm<sup>2</sup> - min). As shown in Figure 1 the evaporative flux of water is relatively constant from 200 to 1200 cm<sup>2</sup> and regression analysis of all the data is statistically (correlation, R<sup>2</sup> = 0.96) expressed as

$$\text{Flux} = 0.20 + 2.04 (\text{area})^{-1}$$

where Flux is mg/cm<sup>2</sup>-min

area is cm<sup>2</sup>

Similar regression of the limited MMH data (Figure 1) expresses the flux as

$$\text{Flux} = 1.64 + 7.05 (\text{area})^{-1}.$$

The evaporation rates of the hydrazine fuels (Table 1) were determined with surface areas of 177 cm<sup>2</sup> and estimate the constant evaporation flux of larger liquid areas within 10-15 percent error.

Increasing liquid pool temperatures causes significant evaporation rate increases (Figures 2 and 3) but difficulties in controlling the actual pool temperature prevented calculating the precise relationship. Although the pool bath temperature varied by less than 1°C, both the actual liquid temperature and room air temperatures changed by as much as 3°C during the course of an experiment.

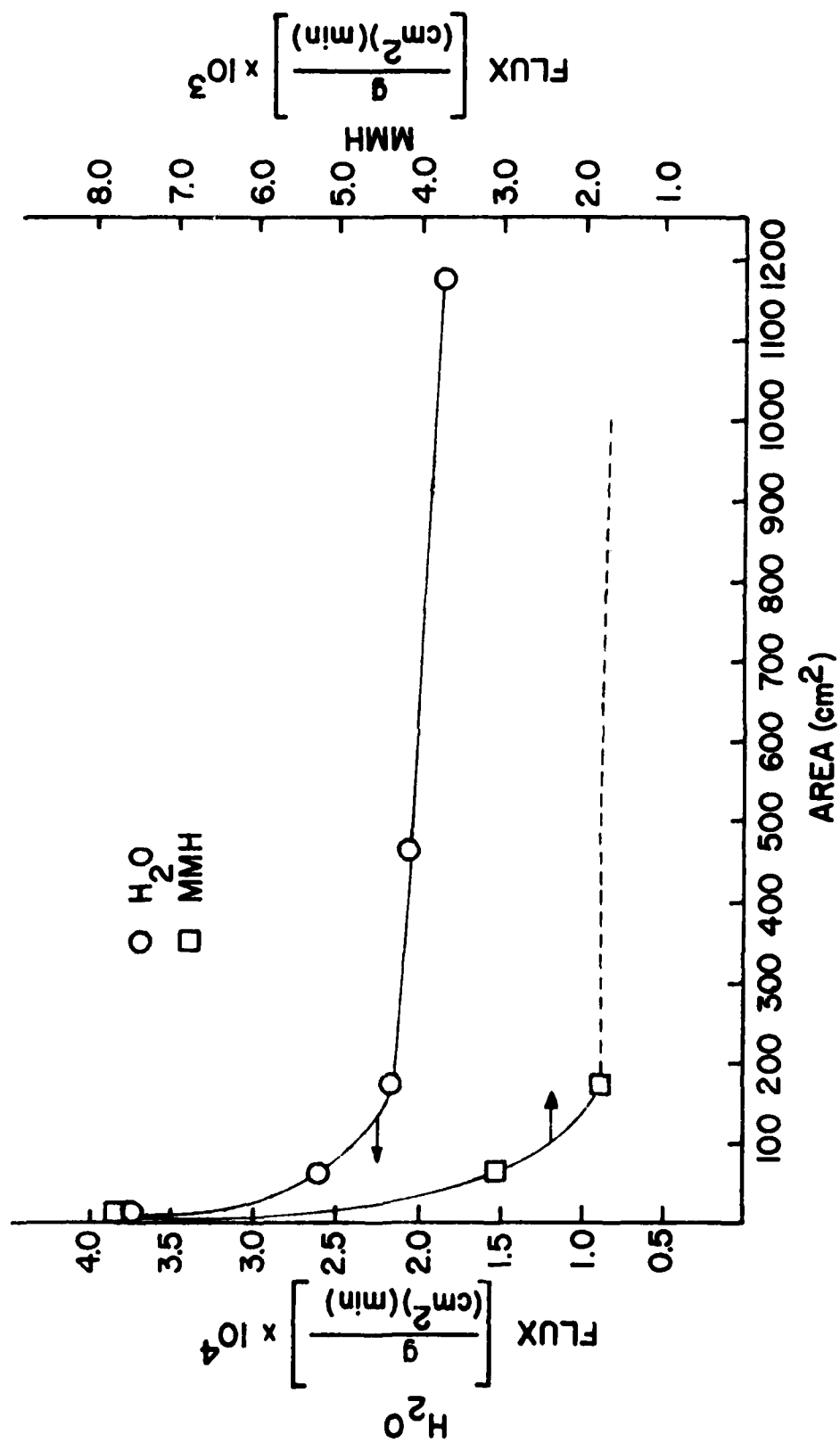


Figure 1. Effect of Surface Area on Flux Rate.

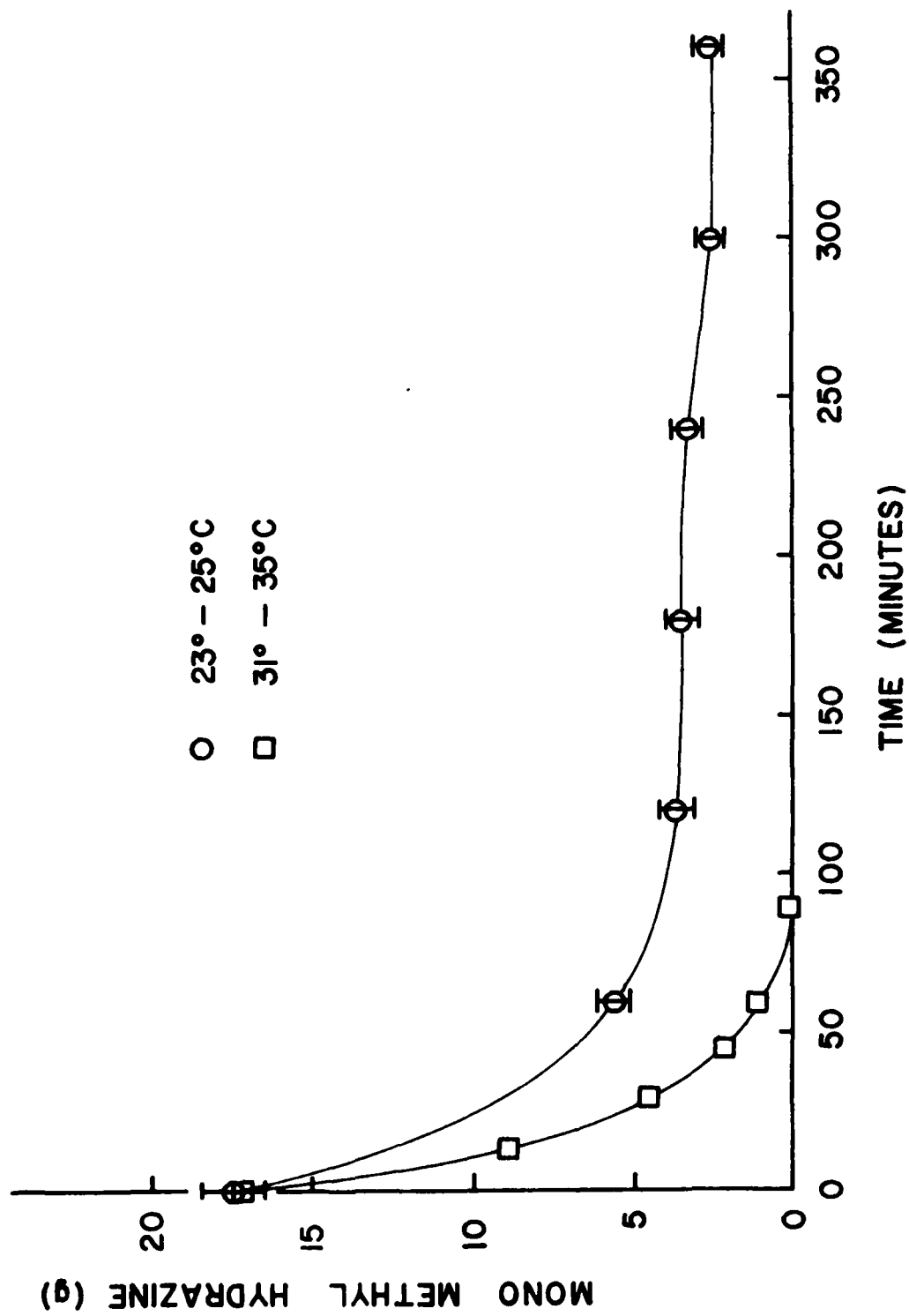


Figure 2. Monomethylhydrazine Evaporation.

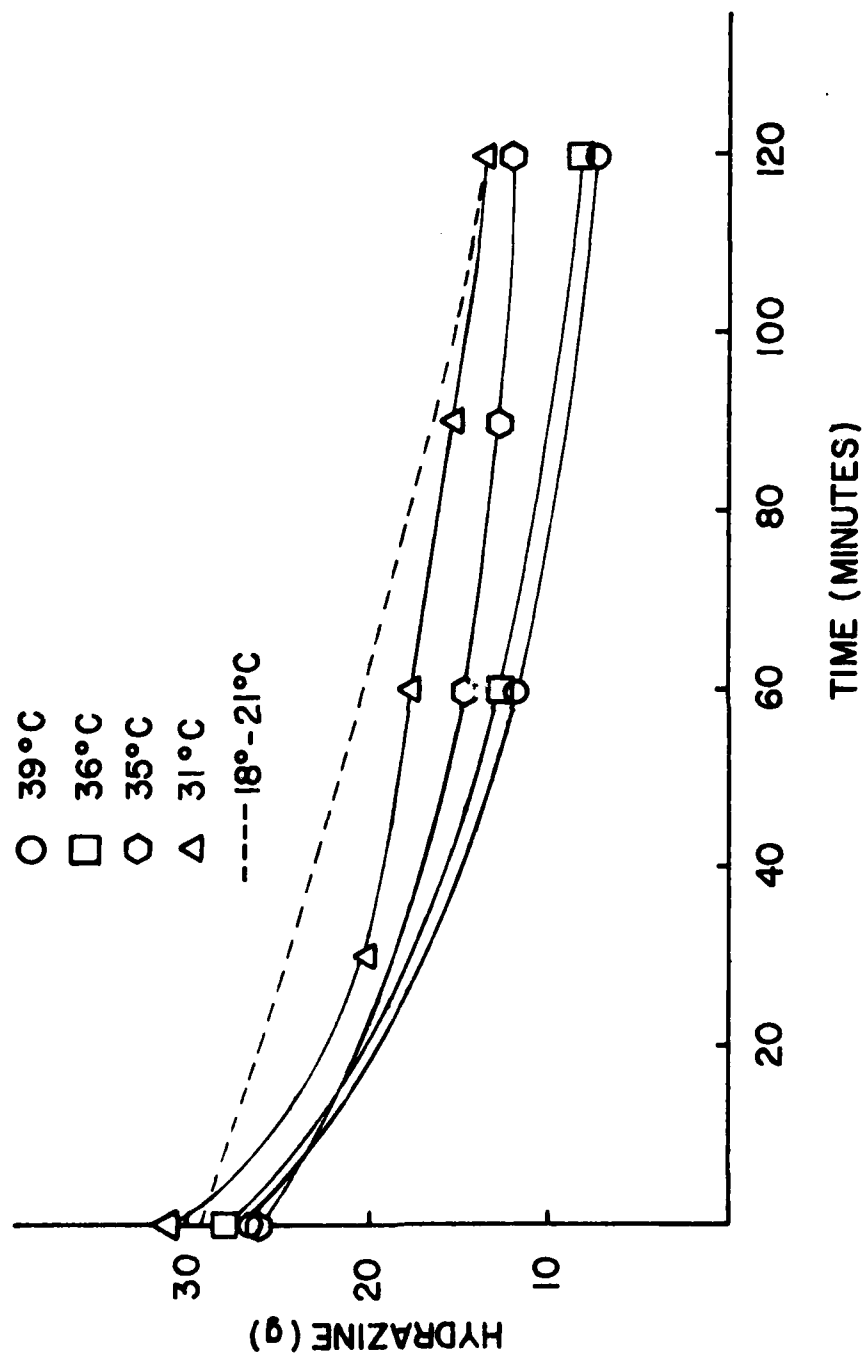


Figure 3. Temperature Effects on Hydrazine Evaporation.

TABLE I. CHEMICAL &amp; PHYSICAL PROPERTIES OF HYDRAZINE FUELS

FUEL	DENSITY (g.cc)	BOILING POINT (°C)	VAPOR PRESSURE (Pa)	EVAPORATION RATE (mg/cm <sup>2</sup> min)	HALF LIFE AIR (hr)	HALF LIFE WATER (days)
Hydrazine (N <sub>2</sub> H <sub>4</sub> )	1.0	114.2	1892.9	0.49	1-10	7
MONOMETHYL- HYDRAZINE (CH <sub>3</sub> NHNH <sub>3</sub> )	0.87	87.7	6598.4	1.7	2-7	10
UNSYM. DIMETHYL- HYDRAZINE (CH <sub>3</sub> ) <sub>2</sub> N <sub>2</sub> H <sub>2</sub>	0.78	62.3	22274.4	13	100	10

Aqueous Decomposition:

Although they are energetic reducing compounds, the hydrazines are remarkably stable in the absence of appropriate catalysts. The data presented in Table 1 demonstrates that for accidental spills complete aqueous decay by oxidation may take several weeks. Aqueous decomposition rates of hydrazine fuels were determined in deionized, distilled water as well as fresh and salt water samples. The rates are similar in natural waters (fresh or marine) and are faster than in distilled water as shown in Figure 4 (for UDMH).

This increased decomposition in natural waters may be due to low concentrations of endogenous metals, such as copper which is known to catalyze the oxidation of hydrazine. Gas chromatographic/mass

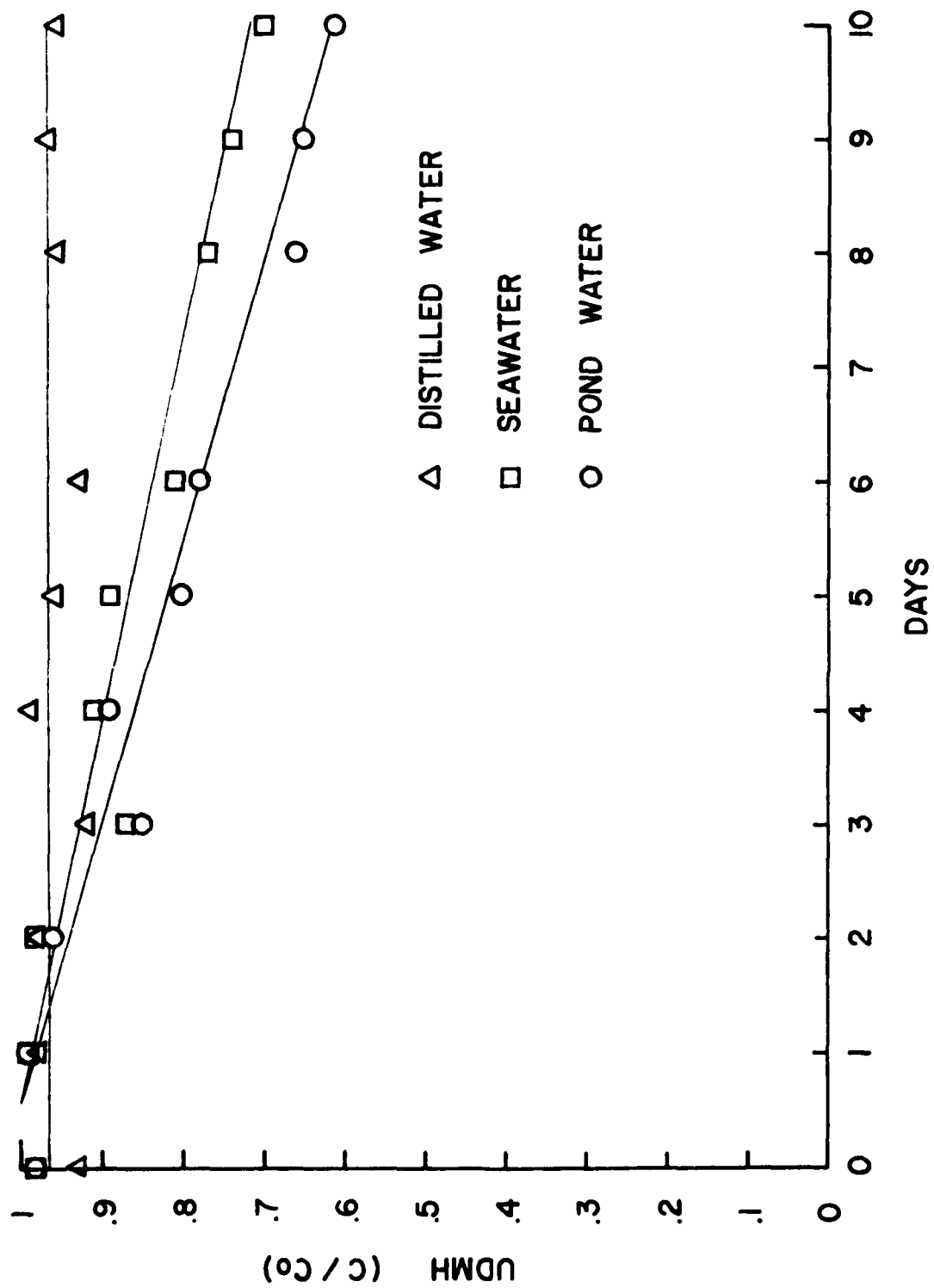


Figure 4. UDMH Aqueous Decomposition

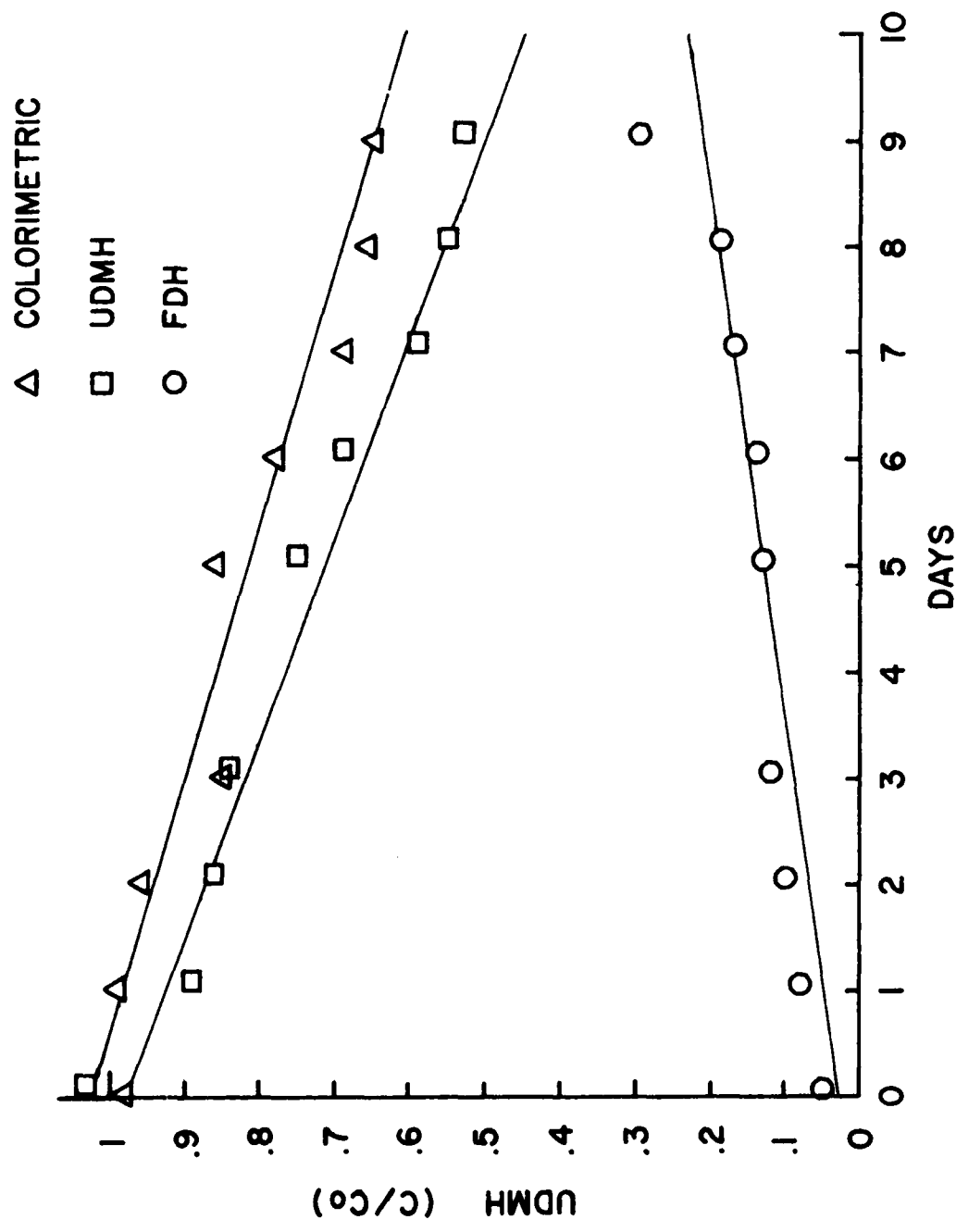


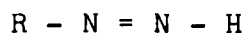
Figure 5. UDMH Decomposition, Pond Water

spectrometric analysis of UDMH decomposition quantitated and identified formaldehyde dimethylhydrazine (FDH) as the major degradation product (Figure 5). Since the colorimetric assays are equally responsive and additive with the hydrazine products, aqueous decomposition rates of the hydrazines determined by GC/MS analysis are slightly faster than those measured by colorimetry. But as these hydrazines have the same relative toxicity as the hydrazines, the aqueous half-lives shown in Table 1 reflect the decomposition rates as measured by colorimetry.

#### Atmospheric Decompositions:

Studies in our laboratory have shown that atmospheric ( $O_2$ ) oxidation of hydrazines is highly dependent on the available chamber surface area and composition of this surface material. Because the decay rate is greatly influenced by these heterogeneous reactions, extrapolation of reaction cell data (Table I) to atmospheric ambient conditions should be made cautiously.

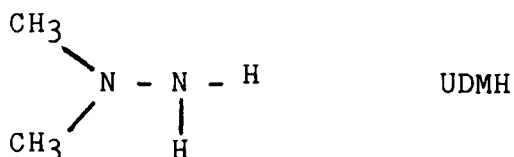
While Hz and MMH exhibit comparable reactivities, UDMH autooxidizes much slower (Table I). This behavior may be indicative of a different decomposition mechanism for UDMH. The major autooxidation products of the hydrazine fuels are listed in Table II. The significant formation of nitrogen from Hz and MMH probably results from a multistep reaction sequence containing a common homologous intermediate, diimide and methyldiimide (from Hz and MMH respectively).



R = H, diimide

R = CH<sub>3</sub>, methyldiimide

The very reactive diimide specie then decomposes to nitrogen and either hydrogen (from Hz) or methane (from MMH). Diimide formation results from the loss of a hydrogen from each of the hydrazine nitrogens. Being unsymmetrically methylated,



UDMH cannot readily achieve this 1, 2 hydrogen loss. Instead loss of two hydrogens from UDMH would result in a charged product, diazene, which could further react through a complex surface reaction to form FDH.

TABLE II. MAJOR AUTOXIDATION PRODUCTS OF HYDRAZINE FUELS

HYDRAZINE	MMH	UDMH
Nitrogen	Formaldehyde Monomethylhydrazone (FMH)	Formaldehyde Dimethylhydrazone (FDH)
	Nitrogen	
	Methane	

### Summary

The use and transport of hydrazine fuels and their toxicity to both humans and lower organisms makes it imperative to understand

their behavior and fate in the environment. Evaporation of spilled fuels is a significant environmental process as these rates measured from 0.5 mg/cm<sup>2</sup>-min for Hz to 13 mg/cm<sup>2</sup>-min for UDMH. It is also apparent that in contrast to their energetic decompositions as fuels, the hydrazines are relatively stable in natural environments. The atmospheric and aqueous half-lives indicate that for accidental fuel releases, autoxidation will not be a significant removal process. Instead environmental fuel concentrations will be controlled by dispersion, dilution, and decomposition by natural or pollutant reactants.

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